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Arsenic	As	74·96	Nickel	Ni	58·68
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Boron	B	11·0	Osmium	Os	190·9
Bromine	Br	79·92	Oxygen	O	16·00
Cadmium	Cd	112·40	Palladium	Pd	106·7
Cæsium	Cs	132·81	Phosphorus	P	31·04
Calcium	Ca	40·07	Platinum	Pt	195·2
Carbon	C	12·00	Potassium	K	39·10
Cerium	Ce	140·25	Praseodymium	Pr	140·6
Chlorine	Cl	35·46	Radium	Ra	226·4
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CCXL.—*Catalysis. Part XVIII.* The Reac...
Both the Ions and the Molecules of A...
Bases and Salts: The Reactions of Alkyl H...
with Phenoxides and Ethoxides.

By JOHN HANSTON SHRODER and SOLOMON FARLEY A...

THE two recent papers by Segaller (T., 1913, **103**, 1154, 11...
the action of alkyl haloids on sodium phenoxide show that ...
reaction velocity increases with dilution, the formula

$$K_v = K_1 + a \log V,$$

used by Hecht, Conrad, and Brückner (*Zeitsch. physikal. ...
1890, **5**, 289), applying equally well to Segaller's results. ...
since the brilliant work of Arrhenius on the ionic theory ...
Ostwald on the relation between the ionisation of acids and ...
activity in ester catalysis, inversion of sucrose and hydr...
acetamide, chemists generally, Kahlenberg (*J. Physical ...
1901, **5**, 339; 1902, **6**, 1) especially, Michael (*Amer. ...
1910, **43**, 322) and Armstrong being notable excepti...
believed that only ions enter appreciably into chemical trans...
tions. Even the known "deviations from the ionic reac...
especially those produced by added salts, were thought to ...
to a change in the ionic reaction by the salts themselves. ...
was pure chance that Arrhenius and Ostwald worked with re...
in which ions are chiefly concerned, and as the "deviati...
the ionic reaction" or "salt catalysis" observed by them
be partly or wholly due to the reactions of the non-ionised e...
lytes, the workers in this laboratory have since 1905 bee...
the theory that both the ions and molecules of acids, base...
salts, must in all cases be examined for activity. John...
Acree in 1907 (*Amer. Chem. J.*, **37**, 410; **38**, 258) bro...
this idea clearly for salts, and in 1908 Shadinger and Acree ...
"We are studying the problem whether acids, bases and salts e...
into these reactions through their ions or molecules, or b...
Besides the discussion of "salt catalysis" (*ibid.*, 1908, **39**,...
we gave the equation (*ibid.*, p. 228) $dx/dt = K_{ions} a (1 ... $ ...
reactions of the ions, as Arrhenius, Ostwald, and all others of
them have done, and then gave (*ibid.*, p. 228) the equa...
$dx/dt = K'_{ions} (1 - a)(1 - x)^2$ for the activity of the "unionise...
acid, base or salt," this idea and equation being the first ...
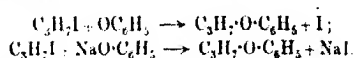contribution to the theory of chemical reactions and the ...

... deviations from the ionic reactions" or "salt catalysis" since Arrhenius' brilliant work in 1885. Before the American Chemical Society in Baltimore, in December, 1908 (*Science*, **30**, 624), one of us stated that: "We see, then, that the question whether the ion or *cation* (simple or complex) or the *molecular form* of a given acid, base, salt or other neutral substance, is the chief constituent transformed directly into the end products depends entirely upon the relative magnitudes of the various constants, and therefore varies widely in the different problems." Our work (*this Chem. J.*, 1912, **48**, 352; 1913, **49**, 116, 127, 345, 369, 474, and earlier papers) has now shown that this new idea of the activity of non-ionised electrolytes is fully as important for chemical reactions as the idea that ions are active. To express reaction velocities completely, we must use the equation

$$K_N = \{K_i a + K_m (1 - a)\}\{1 + (f)C'_{\ldots a}\}.$$

The second term on the right side of the equation represents a factor for "salt catalysis," and the first term gives the activity of ions and molecules in normal solutions having the ionisation and the velocity K_N. This theory has been found to hold in our thirty reactions studied by us in concentrated solutions (N to N 32), as well as in ideal solutions (N 32 to N 2048), these involving the three most important classes of chemical changes, namely, metathesis, pure catalysis and intramolecular arrangement. By this theory we have been able to reinterpret the work of Arrhenius, Ostwald, Conrad and his co-workers, Sen, Tubandt, Stieglitz, Bredig, Goldschmidt, Holmberg, Walker, van Dam, Blanksma and Segaller as reactions of ions and molecules, instead of ions alone. The theory has, moreover, now been accepted and used by Arrhenius (Taylor and Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, Nos. 34, 35, 37), Stieglitz (*J. Amer. Chem. Soc.*, 1912, **34**, 1687, 1689, 1690, 1694; 1913, **35**, 1774), Dawson (T., 1913, **103**, this vol., p. 1093), Goldschmidt (*Zeitsch. Elektrochem.*, 1909, Zeitsch. physikal. Chem., 1910, **70**, 627), Bredig (*Zeitsch. Biochem.*, 1912, **18**, 535, 543; *Zeitsch. physikal. Chem.*, **85**, 129, 170, 211), Holmberg (*Zeitsch. physikal. Chem.*, **84**, 451, 468, 469), Biddle (*J. Amer. Chem. Soc.*, 1914, **36**, and earlier papers), Kilpi (*Zeitsch. physikal. Chem.*, 1913, **86**, and Worley (*Phil. Mag.*, 1914, [vi], **27**, 459), and bids to become generally useful in all reactions involving electrolytes.

Segaller studied the reactions of $N/2$-sodium phenoxide with a series of different alkyl haloids at 42·5° in order to measure their relative chemical activities. Fortunately, he investigated the

action of n-propyl iodide on varying concentrations of sodium phenoxide, and it is this work that interests us at present, and extends our series of investigations with methyl and ethyl iodides at 25° and 35°. Lack of time alone is all that has prevented us from using all the other alkyl haloids in our work on the phenoxides, ethoxides, and urazoles. We have now extended Segaller's data to obtain the reaction-velocities for solutions $N/2$, $N/4$, $N/10$, and $N/20$, and have found by the use of the equation, $K_N = K_i \alpha + K_m(1 - \alpha)$, that his data harmonise excellently with ours and with our theory, both the phenoxide ions and the non-ionised sodium phenoxide seeming to react with propyl iodide, as follows:

$$C_3H_7I + OC_6H_5 \longrightarrow C_3H_7 \cdot O \cdot C_6H_5 + I;$$
$$C_3H_7I + NaO \cdot C_6H_5 \longrightarrow C_3H_7 \cdot O \cdot C_6H_5 + NaI.$$

The following tables show the values of K_i and K_m obtained by us from our own work on methyl and ethyl iodides and sodium, potassium, and lithium phenoxides at 25° and 35°, and from Segaller's work at 42·5°. Because of larger experimental error the values of K_i do not agree as well at 35° as at 25°. The values of α used by us in recalculating Segaller's data were obtained by extrapolation of H. C. Robertson's data for sodium phenoxide at 0°, 25°, and 35°. It is seen that the ratio K_i/K_m for both methyl iodide and ethyl iodide and sodium phenoxide is from 5 to 6 at 25°, and 6 to 7 at 35°, whilst for propyl iodide it is about 17 at 42·5°, and the reaction is almost purely ionic in solutions more dilute than $N/50$. The value for K_i for the phenoxide ion and methyl iodide is about five times as large at 25° and 35° as that for ethyl iodide, which in turn is about three times the value of K_i found for the phenoxide ion and propyl iodide at 42·5°.

Temperature, 25°.

						K_i	k
Sodium phenoxide and methyl iodide				...		0·0282	0·0047
Potassium	,,	,,	,,	,,	...	0·0283	0·0047
Lithium	..	,,	,,	,,	...	0·0287	0·0045
Sodium phenoxide and ethyl iodide				...		0·00551	0·00087
Potassium	,,	,,	,,	,,	...	0·00518	0·00092
Lithium	..	,,	,,	,,	...	0·00534	0·00095

Temperature, 35°.

					K_i	k
Sodium phenoxide and methyl iodide			...		0·0909	0·015
Potassium	,,	,,	,,	...	0·1036	0·0158
Sodium phenoxide and ethyl iodide			...		0·0183	0·0032
Potassium	,,	,,	,,	...	0·0197	0·0033
Lithium	..	,,	,,	...	0·0174	0·0034

Temperature, 42·5°.

			K_i	k
Sodium phenoxide and propyl iodide	...		0·0128	0·00075

Our chief interest in Segaller's work and that of Hecht, Conrad, of Brückner lies in the fact that the change in K_N with dilution fits the equation $K_N = K_1 + a \log V$, as written by Hecht, Conrad, and Brückner. A more general form is

$$K'_N - K_N = a \log (V'/V),$$

which K'_N and K_N represent $V'K_N$ and $V K_N$, the reaction-velocities for the concentrations $1/V'$ and $1 V$, as used in our earlier papers. This equation is purely empirical, has never been on any scientific foundation, and it does not involve the changing ionisation of the ethoxide or phenoxide, because Hecht, Conrad, and Brückner did not consider the possibility of the ionisation of the sodium ethoxide or phenoxide, but spoke of all these substances as non-electrolytes, or "nichtleitende Körper." We have therefore interested ourselves in determining why this simple equation holds so excellently, as it undoubtedly does, for the work of Hecht, Conrad, and Brückner, Segaller, and for that part of ours to which we have applied it.

When we write Conrad's equation as (1) $K'_N - K_N = a \log (V'/V)$, and one of our simultaneous equations as (2) $K_N = K_i a + K_m (1 - a)$ (3) $K'_N = K_i a' + K_m (1 - a')$, and subtract (2) from (3), we get $K'_N - K_N = (K_i - K_m)(a' - a)$. By comparing equations (2) and we get (5) $K'_N - K_N = a \log (V'/V) = (K_i - K_m)(a' - a)$, and this (6) $a = \dfrac{(K_i - K_m)(a' - a)}{\log(V' V)}$ and (7) $a = \dfrac{K'_N - K_N}{\log(V' V)}$. The $a (V'/V)$ of Conrad's equation (1) has a scientific basis, therefore, only if equation (6) actually gives "constants" for a. We have recalculated Segaller's work, and Dr. W. A. Taylor has that of Hecht, Conrad, and Brückner, and we have also applied these also to much of our own work; we find that equations (6) and (7) hold excellently within the experimental errors. Of course the central point hinges on the validity of the relation

$\dfrac{V'}{V} = K$, an empirical equation that holds very well in the

concentrated solutions of a number of electrolytes to which have applied it, whether the electrolyte obeys the Ostwald dilution law or is too "strong" to do so. This equation cannot hold for all concentrations, because the ratio V'/V keeps on changing after complete ionisation is reached, whereas $a' - a$ then is constant. We are investigating all these relations fully. Our extended reports on the work of Segaller, and of Hecht, Conrad, and Brückner, will soon be published by Dr. J. H. Shroder and W. A. Taylor.

seen in tables VI of both sections of the experimental portion that both equations (6) and (7) give very good constants for

a, the two values, 0·00265 and 0·00269, for sodium phenox... ...
propyl iodide at 42·5° agreeing better than the values 0·... ...
0·02594 for sodium ethoxide and methyl iodide at 24°. I... ...
in tables VII of both sections that the values for "K_N calcul...
agree well with those for "K_N found."

It is thus seen that the empirical relation

$$K'_N - K_N = a \log (V'/V)$$

used by Hecht, Conrad, and Brückner, and by Segaller ... ...
relation $K'_N = K_N$ observed by Bredig (*Zeitsch. Elektroche...* ...
10, 582), Tubandt (*Annalen*, 1905, **339**, 41; 1907, **354** ...
1910, **377**, 284), Steger (*Rec. trav. chim.*, 1899, **18**, 13, 4...
by McCombie and Scarborough (this vol., p. 1304), and Mc... ...
Acree (*Amer. Chem. J.*, 1912, **48**, 358; 1913, **49**, 141, ...
the salt catalysis equation, $K_N = K_i a + K_s a^2$, or its equiv... ...
by Arrhenius, Spohr, Euler, Stieglitz and others, are all ... ...
cases that can be converted into our general equation

$$K_N = [K_i a + K_m (1 - a)][1 + (f)C_{\text{sub}}],$$

involving the reactions of both the ions and the non-ionis... ...
of acids, bases, and salts.

Interaction of Sodium Phenoxide and Propyl Iodide at ...

TABLE I.

K_N *Found for Sodium Phenoxide and Propyl Iodide at ...*

Concentration of sodium phenoxide. V.	K_N.	K_N average.	Concentration of sodium phenoxide. V.	K_N K ...
2	0·00280		10	0·00480
	0·00293			0·00475 ...
	0·00305		20	0·00552
	0·00309	0·00297		0·00571 ...
4	0·00369			
	0·00371	0·00370		

TABLE II.

Ionisation of Sodium Phenoxide at 42·5...

V.	a.	$1-a$.
2	0·1826	0·8174
4	0·2400	0·7600
10	0·3265	0·6735
20	0·4065	0·5935

TABLE III.

K_a and K_m Found for Sodium Phenoxide and Propyl Iodide at $42.5°$.

	$K_a.$	$K_m.$
$V = 2 : V = 4$	0·01337	0·000648
$V = 2 : V = 10$	0·01325	0·000673
$V = 2 : V = 20$	0·01264	0·000809
$V = 4 : V = 10$	0·01319	0·000704
$V = 4 : V = 20$	0·01246	0·000932
$V = 10 : V = 20$	0·01185	0·001364*
Average	0·01280	0·000753

* This value was omitted.

TABLE IV.

K_a Calculated and Found for Sodium Phenoxide and Propyl Iodide at $42.5°$.

$V.$	$K_a.$	K_a calculated.	Error, per cent.
2	0·00297	0·00295	+ 0·7
4	0·00370	0·00364	+ 1·6
10	0·00478	0·00469	+ 1·9
20	0·00562	0·00565	0·5

TABLE V.

Per Cent. of Reaction Due to Ions and to Molecules.

Concentration of sodium phenoxide V.	Per cent. of reaction due to a K_a.	Per cent. of reaction due to $(1 - a)K_m$.
2	79·14	20·86
4	84·40	15·60
10	89·10	10·90
20	92·09	7·91

TABLE VI.

a Found for Sodium Phenoxide and Propyl Iodide at $42.5°$.

	$a = \dfrac{K_a' K_a}{\log(V'/V)}$	$a = \dfrac{(K_a' K_m)(a' a)}{\log(V'/V)}$
$V = 2 : V = 4$	0·002425	0·002297
$V = 2 : V = 10$	0·002589	0·002480
$V = 2 : V = 20$	0·002650	0·002698
$V = 4 : V = 10$	0·002713	0·002618
$V = 4 : V = 20$	0·002746	0·002870
$V = 10 : V = 20$	0·002789	0·003205
Average	0·00265	0·00269

TABLE VII.

K_x *Found,* K_x *Calculated [obtained by using "a" in the f...*
$K'_N = K_N + a \log (V'/V)$], *and Percentage Error*

V.	K_x found.	K_x calculated. for $a = 0.00265$.	Error in per cent.	K_x calculated. for $a = 0.00269$.	...
2	0.00297	0.002970	0.00	0.00297	...
4	0.00379	0.003767	−1.77	0.00378	...
10	0.00478	0.004820	0.83	0.00485	...
20	0.00562	0.005620	0.00	0.00566	...

Interaction of Sodium Ethoxide and Methyl Iodide ...

TABLE I.

K_N *Found for Sodium Ethoxide and Methyl Iodide ...*

Concentration of sodium ethoxide	$K_{..}$	Concentration of sodium ethoxide	k
1	0.05512	20	0.08xx
2	0.06276	40	0.0648x
5	0.07182	80	0.102x
10	0.07950		

TABLE II.

Ionisation of Sodium Ethoxide at 24°.

V.	α.	1 − α.	V.	α.	1 − α
1	0.1470	0.8530	20	0.5075	0.44x
2	0.2346	0.7654	40	0.6040	0.3xx
5	0.3335	0.6665	80	0.7030	0.2xx
10	0.4170	0.5830			

TABLE III.

K_t *and* K_m *Found for Sodium Ethoxide and Methyl Iodide ...*

V.			$K_{..}$	$K_{..}$
V	1 : V	2	0.1294	0.04230
V	1 : V	5	0.1215	0.04191
V	1 : V	10	0.1312	0.0418x
V	1 : V	20	0.1304	0.04212
V	1 : V	40	0.1284	0.04241
V	1 : V	80	0.1274	0.04261
V	2 : V	5	0.1328	0.0412x
V	2 : V	10	0.1330	0.0412.
V	2 : V	20	0.1306	0.04191
V	2 : V	40	0.1281	0.0426x
V	2 : V	80	0.1273	0.0429x
V	5 : V	10	0.1331	0.04114
V	5 : V	20	0.1297	0.0428x
V	5 : V	40	0.1276	0.0438x
V	5 : V	80	0.1267	0.0443x
V	10 : V	20	0.1275	0.0453x
V	10 : V	40	0.1262	0.0460x
V	10 : V	80	0.1258	0.0463x
V	20 : V	40	0.1253	0.0473x
V	20 : V	80	0.1255	0.0472x
V	40 : V	80	0.1256	0.0470x
		Average	0.1287	0.04334

TABLE IV.

K_s *Calculated and Found for Sodium Ethoxide and Methyl Iodide at* 24°.

$K..$	K_s calculated.	Error in per cent.	$V.$	$K..$	K_s calculated.	Error in per cent.
0.05512	0.05605	-1.68	20	0.08696	0.08676	-0.23
0.06276	0.06352	-1.21	40	0.09448	0.09498	0.52
0.07182	0.07194	-0.16	80	0.1022	0.1034	1.17
0.07950	0.07905	+0.57				

TABLE V.

Per Cent. of Reaction Due to Ions and to Molecules.

Concentration of sodium ethoxide	Per cent. of reaction due to aK_s	Per cent. of reaction due to $(1-a)K..$	Concentration of sodium ethoxide	Per cent. of reaction due to $aK.$	Per cents of reaction due to $(1-a)K..$
1	33.75	66.25	20	75.28	24.72
2	47.53	52.47	40	81.84	18.16
5	59.66	40.34	80	87.51	12.49
10	67.89	32.11			

TABLE VI.

K_s *Found for Sodium Ethoxide and Methyl Iodide at* 24°.

a	$\dfrac{K_s K_s}{\log(V/V')}$	a	$\dfrac{(K_s-K..)(a-a)}{\log(V/V')}$
V 1 : V = 2	0.02538		0.02478
V 1 : V = 5	0.02388		0.02271
V 1 : V = 10	0.02438		0.02299
V 1 : V = 20	0.02447		0.02359
V 1 : V = 40	0.02456		0.02551
V 1 : V = 80	0.02474		0.02921
V 2 : V = 5	0.02276		0.02116
V 2 : V = 10	0.02393		0.02221
V 2 : V = 20	0.02420		0.02729
V 2 : V = 40	0.02438		0.02837
V 2 : V = 80	0.02431		0.02923
V 5 : V = 10	0.02551		0.02328
V 5 : V = 20	0.02515		0.02464
V 5 : V = 40	0.02509		0.02550
V 5 : V = 80	0.04523		0.02622
V 10 : V = 20	0.02478		0.02560
V 10 : V = 40	0.02488		0.02944
V 10 : V = 80	0.02513		0.02697
V 20 : V = 40	0.02498		0.02730
V 20 : V = 80	0.02531		0.02768
V 40 : V = 80	0.02564		0.02800
Average	0.02470		0.02594

TABLE VII.

K_N *Found,* K_N *Calculated* {*obtained by using* "a" *in the* $E_{...}$ $K'_N = K_N + a \log (V'/V)$}, *and Percentage Error.*

V.	K found.	K, calculated for $a = 0.02470$.	Error. per cent.	K, calculated for $a = 0.02594$.	
1	0·05512	0·05458	+0·99	0·05372	
2	0·06276	0·06199	+1·24	0·06150	
5	0·07182	0·07182	-0·00	0·07182	
10	0·07950	0·07948	+0·03	0·07963	
20	0·08696	0·08669	-0·31	0·08743	
40	0·09448	0·09412	+0·36	0·09524	
80	0·10220	0·10159	-0·59	0·10305	

Conclusions.

(1) It has been shown that the work of Hecht, Conrad, and Brückner on the interaction of methyl iodide and sodium ethoxide at 24°, and that of Segaller on the interaction of n-propyl iodide and sodium phenoxide at 42·5°, harmonises with our own along these lines. Their data give constants for K_i and K_m, substituted in the equation $K_N = K_i a + K_m (1 - a)$, and give excellent evidence that both the ethoxide and phenoxide ions, as well as the non-ionised sodium ethoxide and sodium phenoxide molecules, react with the alkyl haloids. The values K_i and K_m 0·04354 are found for methyl iodide and sodium ethoxide at 24°, whereas $K_i = 0.0128$ and $K_m = 0.000753$ are found for sodium phenoxide and propyl iodide at 42·5°.

(2) Hecht, Conrad, and Brückner, and Segaller, found that the reaction-velocities can be expressed accurately by the equation $K'_N = K_N + a \log (V'/V)$, an equation which does not take into consideration the changing values of the ionisation of the ethoxides and phenoxides. We have found that this equation harmonises with our theory and the equation $K_N = K_i a + K_m (1 - a)$, and because of the fact that the changes in volume, ionisation, and reaction velocity correspond closely with the equations

$$a = \frac{K_N - K_N}{\log (V'/V)} = \frac{(K_i - K_m)(a' - a)}{\log (V'/V)}.$$

We are indebted to the Carnegie Institution of Washington for aid in this work.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

CCXLI.—*The Limits of Inflammability of Mixtures of Methane and Air.*

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

IN a recent communication (this vol., p. 1859) Coward and Brinsley suggested that "inflammability must be regarded as a specific property, either present or absent, of any given gaseous mixture under definite conditions of temperature and pressure" (p. 1884); independent of the shape and size of the vessel containing it, and dependent also of the nature of the means used for ignition in the first place" (p. 1861).

On the basis of this definition, a "criterion" of inflammability is put forward, which, stated briefly, demands that the true "limit-mixture" must be regarded as that in which flame can be propagated upwards—indefinitely.

It is well known that mixtures of methane, for example, and air have different limits of inflammability, both higher and lower, dependent on the direction in which the flame has to travel.* Coward and Brinsley were probably led to their choice as to what constitutes a true "limit-mixture" by consideration of the fact that a smaller percentage of inflammable gas is required (they are only with the lower-limit) for upward than for downward propagation of flame, and by the belief that the experimental conditions specified by them disclosed the least quantities of the combustible gases, hydrogen, methane, and carbon monoxide, that are capable of forming with air mixtures in which self-propagation of flame can take place.

It does not seem to us desirable so to restrict the use of the term "limit-mixture." The most important industry in which knowledge of the limits of inflammability of gaseous mixtures is required is coal-mining. The occurrence of fire-damp in mines constitutes, as well known, one of the gravest dangers to the industry; not so much, it is believed, because of the possibility of widespread explosions taking place in fire-damp and air mixtures extending through the workings, modern legislation regarding the ventilation of mines having rendered such occurrences exceedingly unlikely, but because a local accumulation of fire-damp, forming an explosive mixture with the air, may become ignited and transmit flame to

---

* This fact has been emphasised by Professor Enrique Hauser in a brochure entitled "Leçons sur le grisou" (Madrid, 1908). Hauser has summarised the best results given by various experimenters for the limits of inflammability of methane air mixtures, and has offered an explanation of the differences.

any fine coal dust that may be deposited on the roadways may produce a widespread coal-dust explosion.

Legislation has attempted to deal also with this danger, stipulating that frequent analyses shall be made of the air of mine roadways and workings, and precautions taken to prevent the percentage of methane contained in the air from exceeding certain minimum. Despite precautions, accumulations of fire-damp usually near the roof, sometimes occur; and, should sufficient fire-damp mingle with the ventilating current and by some means encounter a sufficiently intense source of heat, what is technically called a "local ignition" may occur. In the majority of cases no damage or loss of life is caused by these "local ignitions," which usually take the form of a slowly-moving flame near the roof.

Such cases of the propagation of flame in fire-damp air mixtures are those most frequently reported. It will be realised that danger lies in the existence, over a considerable length of roadway, of a mixture in which a flame can travel horizontally. A serious danger arises when, as has been known to happen, a fall of part of the roof liberates, and distributes in the ventilating current, a quantity of fire-damp that has accumulated in cavities above the roof.

A uniform inflammable mixture of fire-damp and air rarely occurs throughout any considerable area of a coal mine, but there is an instance when a disused heading (or cul-de-sac), in which air was practically stagnant, was slowly fed with fire-damp issuing from the neighbouring strata until, when the fact was discovered, the whole heading had become uniformly filled with a gas containing 6 per cent. of methane. It has sometimes happened also, that the slow ventilating current travelling through a leading from a goaf (or worked-out place) has been found to be inflammable mixture, uniform in composition through its extent. In such cases the dangerous "limit-mixtures" are those will allow of self-propagation of flame throughout the mixture, whether ignition occurs at the roof, floor, or central roadway.

The fire-damp of British mines consists of methane mixed with varying proportions of nitrogen; also, carbon dioxide, traces of carbon monoxide and ethylene may be present, and, in rare cases, traces of ethane have been detected.

This paper records the results of determinations of the higher and lower-limits of inflammability of mixtures of pure methane with air, and shows how the compositions of the limit-mixtures
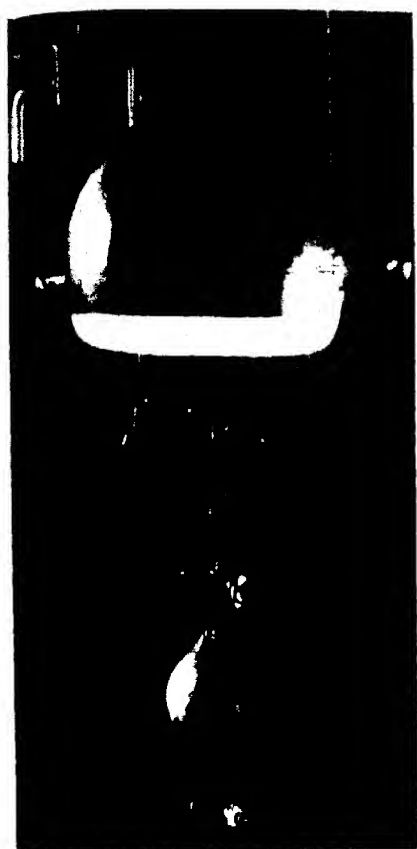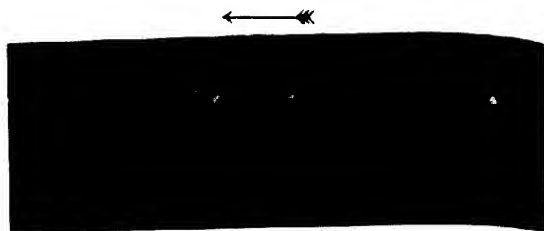
Fig. 2.
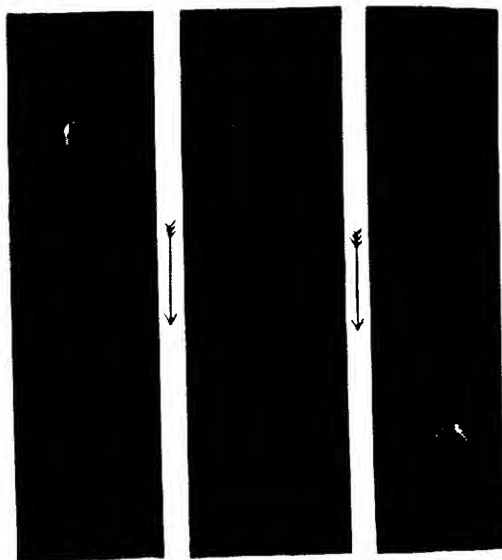
... dependent on the manner in which ignition is effected.[*] These results are as follows:

	Methane, per cent.	
	Lower limit.	Higher limit.
Central ignition in large globe.........	5·6	14·8
Vertical tube, closed at both ends:		
(a) Ignition at bottom [*]	Not less than 5·40	Not more than 14·8
(b) Ignition at top [†]..................	6·0	13·4
Horizontal tube, closed at both ends:		
Ignited at one end	{ 5·4 (flame travels only along top of tube) 5·6 (methane all burnt) }	14·3

[*] Coward and Brinsley obtained what appeared to be a self-propagating flame in a mixture containing, according to analysis, 5·3 per cent. of methane. They were led to reject the experiment.

[†] The determinations made by Hauser (*loc. cit.*), using the Le Chatelier burette (upward propagation of flame), were: lower limit 6·05 per cent., higher limit ... per cent. methane. Hauser obtained pure methane from aluminium carbide.

The manner in which the flame travels in the different mixtures is by no means the same, and an attempt has been made to indicate the more striking differences by diagrams. Fig. 1 represents the flame travelling upwards in a closed tube (6 cm. in diameter) containing a 5·4 per cent. methane air mixture, and Fig. 2 the flame travelling horizontally in a like mixture. Figs. 3 and 4 illustrate stages in the progress of the flame downwards in a closed tube through a mixture containing 6·0 per cent. of methane.

When an electric spark is passed at the bottom of a closed vessel containing methane air mixtures with 5·0, 5·1, 5·2, etc., per cent. methane, flares of flame are produced which travel distances increasing with the percentage of methane, until with 5·4 per cent. methane present the distance of travel reaches 2 metres in a tube 2 metres long. It is possible that the flame in a 5·4 per cent. mixture might travel upwards more than 2 metres; it might travel indefinitely, and, on the other hand, it might die out after a distance of 3 metres or less. Since it is obviously impossible to devise a crucial experiment to test this point, it must suffice to record that the lower-limit mixture for upward propagation of flame contains not less than 5·4 per cent. of methane. The flame in mixtures containing 5·35 per cent. of methane, contained in a vertical glass tube 6 cm. in diameter, never exceeded a distance of about 50 cm.; in 5·3 per cent. and 5·25 per cent. mixtures the flame travelled 40 cm. and 30 cm. respectively.

It will be seen in Fig. 2 that the flame travelling horizontally in

[*] The influence of added nitrogen on the limits, as determined by central ... a large globe, is described in a subsequent paper.

a 5·4 per cent. mixture occupies only the upper quarter of the containing vessel, and analysis of the mixture left 6 cm. in diameter after the flame had travelled along it showed to contain 3·25 per cent. of methane. When a tube 10 cm. diameter was used, 3·9 per cent. of methane remained in the products of combustion. Presumably, if a large room were filled with such a mixture and a light applied at some point near the floor, a column of flame would travel upwards from the point of ignition to the roof and spread along the upper portion of the room.

It may not be generally known that when a slow current of air containing between 4 and 5 per cent. of methane passes over a small flame, such as that of an oil lamp, the cap or aureole that ordinarily forms round the lamp-flame may become detached and travel along with the current. Similarly, if a slow current of air containing 3 or 4 per cent. of coal gas is allowed to ascend a vertical tube, and a succession of electric sparks passed at the bottom, small caps of flame can be caused to pass from end to end of the tube, only a fraction of the mixture being burnt.

Of a like nature are such mixtures of hydrogen and air as cause "balls" of flame to travel (perhaps indefinitely) upwards through them with the convection currents in the manner described by Coward and Brinsley.

From the practical point of view such mixtures are not in themselves dangerous, but they are potentially dangerous in that they could convey flame to richer mixtures.

From the scientific point of view it is of interest to know that such curious flames can be produced, but the doubt must always remain whether actually "indefinite" propagation of flame can take place in the mixtures that exhibit them; and the fact that chemical reaction proceeds in but a small portion of the gaseous mixture, renders it difficult to employ for comparative measurements the "criterion" of inflammability adopted by Coward and Brinsley.*

* It should be noted that, making use of their criterion, Coward and Brinsley decided upon 4·1 per cent. as the lower limit percentage of hydrogen (3·8 per cent. of hydrogen remaining in the mixture after the flame had passed). Dixon and Crofts (this vol., p. 2047) have obtained the following as the ignition temperatures of various mixtures of hydrogen and oxygen:

$$2H_2 + O_2 \quad \ldots\ldots\ldots\ldots \quad 526°$$
$$2H_2 + 2O_2 \quad \ldots\ldots\ldots\ldots \quad 511$$
$$2H_2 + 8O_2 \quad \ldots\ldots\ldots\ldots \quad 478$$
$$2H_2 + 16O_2 \quad \ldots\ldots\ldots\ldots \quad 472$$
$$2H_2 + 32O_2 \quad \ldots\ldots\ldots\ldots \quad —$$

The last mixture, which contained 5·88 per cent. of hydrogen, could not be ignited, although five experiments were made in which the temperature was

It may be remarked that if the object of their criterion of inflammability is to specify the least quantity of inflammable gas that is capable of propagating flame, that object is not gained. For when a mixture of methane and air containing 5 per cent. of methane, enclosed in a 4 litre globe, is strongly agitated by revolving a small fan therein, and an electric spark passed at the centre of the globe, flame travels rapidly throughout the mixture, all the methane being burnt. The lower limit of inflammability of "agitated" mixtures of methane and air could therefore be stated to be 5·0 per cent., or possibly less with more greatly agitated mixtures.

The flame travelling downwards in a 6·0 per cent. mixture, depicted in Figs. 3 and 4, and the flame started centrally in a 5 per cent. mixture contained in a large globe, both burn the methane completely. In both cases the line of demarcation between a mixture that will propagate flame and one that will not is sharply fixed.[*]

For the latter reason, as well as for their convenience, the criterion of inflammability for downward propagation, used by Le Chatelier and universally applied by French mining engineers in the measurement of fire-damp; and for propagation throughout globe, adopted by several investigators, would seem to commend themselves for such comparative measurements as a study of the propagation of flame in gaseous mixtures may demand.

EXPERIMENTAL.

The methane used was prepared from aluminium carbide, and separated from traces of acetylene by passing through ammoniacal cuprous chloride, and from hydrogen by passing slowly over reduced palladium precipitate heated at 90°. It contained 5? per cent. of methane.

The explosion-vessels were glass cylinders, sealed at each end,

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at 550°, 600°, 700°, 1000°, and 1700° respectively. Dixon and Crofts considered that the point of inflammability had been passed in the last mixture, but they noted that combustion occurred of part of the mixture.

[*] The following determinations of the lower-limits, downward propagation, were made by Mr. A. Whitaker. With mixtures containing, according to analysis, 6·01 and 6·01 per cent. of methane, flame was propagated throughout the mixture in a closed tube 7 cm. in diameter and 160 cm. long. With 5·99, 5·98 and 5·?? per cent. of methane the flame travelled 12 or 15 cm. only.

A mixture of mixture sufficient for two experiments was made containing 6·00 per cent. of methane. After one experiment, in which propagation of flame was effected, sufficient air was added to the remainder of the mixture to reduce the percentage of methane to 5·99; flame travelled downwards only 15 cm. in this case.

6 cm. in diameter and 2 metres long. They were fitted with
platinum firing points at one end and at the other with a two-
way tap, through which the mixtures to be experimented with
were introduced after the cylinders had been exhausted. The
mixtures were made over glycerol and water in graduated
gas-holders, and were all analysed before use.

LANMEALS,
CUMBERLAND.

CCXLII.— The Propagation of Flame in "Limit" Mixtures of Methane, Oxygen and Nitrogen.

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

IN a previous communication (T., 1911, **99**, 2013) we argued that a
"lower limit" mixture (and, similarly, a "higher-limit" mixture)
is "one such that a given volume must, under the conditions of
combustion, evolve just sufficient heat to raise an equal volume to
its ignition-temperature."

According to this view, during the propagation of flame in a
"limit" mixture a balance is struck between heat generated by
combustion and heat employed in starting combustion, together
with heat "lost" by conduction and radiation.

Theoretically, provided that the amount of energy imparted to
the system by the initial source of ignition—an electric spark, for
example—is small, so that no appreciable impetus to the propaga-
tion of flame occurs near the source of ignition, flame should travel
throughout a true limit mixture at a uniform speed. Experiments,
to be described at a later date, establish the correctness of this
supposition.

Further, it seems probable that the speed of travel of flame will
be the same in all limit mixtures that comprise the same constitu-
ent gases. Experiments show this to be the case so far as limits of
propagation in mixtures of methane, oxygen, and nitrogen are
concerned.

Limit mixtures thus offer several advantages for the study of the
manner of propagation of flame in gaseous mixtures.

This paper contains the results of a series of determinations of
the amounts of methane required to form higher- and lower-limit
mixtures with various "atmospheres" ranging between air (21
per cent. of oxygen) and a mixture of air and nitrogen containing
13·45 per cent. of oxygen.[*]

* The results of preliminary experiments, obtained during the early part of
1913, were communicated to the institution of Mining Engineers (T., 1913, 44, 44

The lower-limit mixtures contained a minimum of 5·6 per cent. of methane (when air was used) and a maximum of 6·45 per cent. (when the 13·45 per cent. oxygen "atmosphere" was employed). The minimum value for the higher-limit mixtures was 6·7 per cent. of methane (with the 13·45 per cent. of oxygen "atmosphere") and the maximum value 14·8 per cent. (with air).

The compositions were thus determined of a number of limit mixtures containing widely different proportions of the same three gases, methane, oxygen, and nitrogen—from which calculations of the heat balances could be made with a reasonable expectation

Fig. 1.

Oxygen in limit mixtures—per cent.
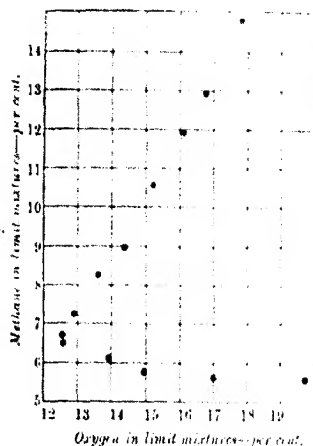
that although errors in calculating the specific heats of the gases and the ignition-temperatures of the mixtures might render the values not strictly accurate, the relative values would be correct.

The results obtained showing the percentages of methane that form limit mixtures with the different "atmospheres" can conveniently be given in the form of a diagram (Fig. 1).

In this diagram percentages of methane are plotted against

percentages of oxygen in the limit mixtures. The different atmospheres," with the percentages of methane required in each case to form higher- and lower-limit mixtures, are as follows:

Atmosphere.		Methane, per cent.	
Oxygen.	Nitrogen.	Lower-limit.	Higher limit.
20·90	79·10 (air)	5·60	14·82
19·22	80·78	—	12·92
18·30	81·70	—	11·91
17·00	83·00	5·80	10·55
15·82	84·18	5·83	8·98
14·86	85·14	6·15	8·34
13·90	86·10	6·35	7·26
13·45	86·55	6·50	6·70
13·25	86·75	No mixture capable of propagating flame

It will be seen that as the oxygen-content of the atmosphere is reduced the higher- and lower-limits come closer together, and with 13·45 per cent. of oxygen only mixtures containing between 6·50 and 6·70 per cent. of methane are capable of propagating flame. A mixture of methane with an atmosphere containing 13·25 per cent. of oxygen is incapable of propagating flame.

Presumably the true "extinctive" atmosphere for methane, the atmosphere in which a jet of methane, however perfectly aerated, would be just unable to burn—contains between 13·45 and 13·25 per cent. of oxygen.[*]

It may be noted that Haldane and Atkinson, who were the first to work on this subject (*Trans. Inst. Min. Eng.*, 1895, 8, 4) found that natural fire-damp could form an inflammable mixture with oxygen and nitrogen when the oxygen present had been reduced to between 12 and 13 per cent. The higher and the limit mixtures of pure methane with the 13·45 per cent. oxygen atmosphere, according to our experiments, contain 12·55 and 1·... per cent. of oxygen respectively.

The general equation representing the heat balance during the spread of flame in a limit mixture is as follows:

$$(c'M + c''P)(T - t) + q = xQ \quad . \quad . \quad . \quad .$$

where c', c'' represent the specific heats of the mixture (M) and the products of combustion (P) respectively, each at the ignition temperature (T), t being the initial temperature of the mixture, q represents heat dissipated (by conduction and radiation), and xQ heat evolved by the combustion of x parts of the combustible gas.

When methane is the combustible gas the calculations are complicated by the fact that combustion is incomplete. Approximate

* The extinctive atmosphere for methane is usually regarded as containing 17 per cent. of oxygen; and the "residual" atmosphere—that in which a methane flame has burnt to extinction—as containing about 15 per cent. of oxygen.

quantities of carbon monoxide occur in the products of combustion
of the lower-limit mixtures, whilst with some of the higher-
limit mixtures combustion is mainly to carbon monoxide, hydrogen,
and steam, and the "water gas reaction" proceeds as the products
...

Consequently, in order to calculate the heat balance it is
necessary to analyse samples of the products of combustion as soon
as they are formed—before secondary reactions, which can play
a part in the propulsion of flame through the mixture, have taken
...

This was done so far as practicable by withdrawing and cooling
very small samples of the "flame gases" whilst the flames were
passing through the mixtures (which were contained in large
globes), in the manner described in the experimental part of
this paper.

The analyses of these gases show a regular relationship between
the ratios O_2:CH_4 in the original mixtures and the proportions of
methane that burn completely to form carbon dioxide and steam.

In the higher-limit mixtures the ratio O_2:CH_4 varied from a
minimum of 1·20 (in the mixture with air) to a maximum of 1·87
(the mixture with the 13·45 per cent. oxygen "atmosphere").
The proportion of the methane burned in the former mixture to
carbon dioxide and steam was 32·2 per cent.; in the latter mixture
to 83·0 per cent. The results have been summarised as follows:

Oxygen-content of atmosphere.	Ratio O_2/CH_4 in higher limit mixture.	Proportions of methane burned to carbon dioxide and steam.
20·90 (air)	1·20	32·2
19·22	1·29	37·8
18·30	1·35	42·6
17·00	1·44	49·0
15·82	1·60	59·0
14·86	1·62	64·5
13·90	1·77	77·4
13·45	1·87	83·0

As the proportion of oxygen to methane is increased, more and
more of the latter is completely burned. With a ratio O_2:CH_4 = 1·50
half the methane burns to carbon dioxide and half to carbon
monoxide, whilst when the oxygen present is less than one and
a half times the methane present the main reaction is represented
by the equation:

$$CH_4 + O_2 = CO + H_2 + H_2O.$$
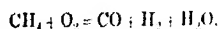
In comparison with these results those obtained by Bone and
Wheeler with mixtures of methane and oxygen in equal propor-
tions may be quoted (T., 1906, **89**, 676). The percentage composi-
tion of the gaseous products of combustion (no carbon was

deposited) averaged: CO_2, 6·3; CO, 41·9; H_2, 50·8, CH...
Commenting on these results, Bone and Drugman say has
been shown that, below the ignition-point, methane burns, form
at an early stage steam and formaldehyde.   The process may
probably be best expressed as follows:

$$CH_4 \longrightarrow CH_3 \cdot OH \longrightarrow CH_2(OH)_2 \longrightarrow CH_2O + H_2O, \text{ etc.}$$
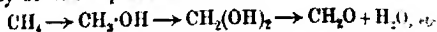
"At high temperatures the formaldehyde would certainly decom
pose into carbonic oxide and hydrogen, so that in any gas
combustion we should obtain:

$$CH_4 + O_2 = \overbrace{CO + H_2} + H_2O.$$
$$\qquad\qquad CH_2O$$
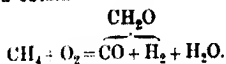
"The 6 per cent. of carbon dioxide formed in our experiment
would obviously arise by the secondary interaction of steam as
carbonic oxide in the flame."

As a general conclusion from our results, we hold the view
that the essential reaction in the propagation of flame in the
limit mixtures is that responsible for the formation of carbon
monoxide, hydrogen, and steam in equal volumes.

The heat evolved by this reaction is probably almost equal
divided between the products of combustion of one layer of
mixture and the adjoining unburnt "layer"; it is, however, suffi
cient to raise the unburnt layer to its ignition-temperature. Follow
ing rapidly upon this reaction, some of the carbon monoxide and
hydrogen is burned, the proportion depending upon the oxygen
concentration. The additional heat added to the system in the
latter manner enables the nearest unburnt layer to attain its
ignition-temperature.

Finally, as the burnt gases cool, the water-gas reaction came
into play, as is shown by comparison of the analyses of the "flame
gases" and "final gases" for the same mixture (compare also
"The Water-Gas Equilibrium in Hydrocarbon Flames," by G.I.
Andrew, this vol., p. 444).

Assuming this to be the correct interpretation of the sequence of
events, calculation of the heat balance of each mixture was
made, using the data supplied by the analyses of the flame gases.

Calculation having been made of the percentages by volume
of the constituent gases of the mixture composed of equal volumes
of burnt and unburnt gases, equation (1) can be put in the form

$$(c_{o_2}A + c_{CH_4}B + c_{N_2}C + c_{CO_2}D + c_{CO}E + c_{H_2}F + c_{H_2O}G)(T - t) =$$
$$xQ + x'Q',$$

c_{o_2}, c_{CH_4}, etc., being the specific heats of the respective gases
the temperature $T - t$, and A, B, etc., the percentages by which
those gases. Of the methane burned, x grams form carbon and

of steam, the heat evolved by the reaction being Q calories per gram; and r' grams form carbon monoxide, hydrogen, and steam, the heat evolved by the reaction being Q' calories per gram.*

Some doubt attaches to the value which should be assigned in each case to T, the ignition temperature of the mixture. Tables of "ignition-temperatures" of various gases do not, in the majority of cases, afford information as to the percentage composition of the mixture formed by the combustible gas with air (or oxygen) when ignition occurs. Thus, the experiments of Dixon and Coward (T., 1909, **95**, 514), in which a heated jet of the combustible gas was allowed to flow into a heated atmosphere of air or oxygen, only determined for each gas the ignition temperature of a mixture having (presumably) the lowest ignition temperature, without showing the composition of that mixture.

In a recent paper by Dixon and Crofts (this vol., p. 2036) the various ignition-temperatures of different mixtures of hydrogen and oxygen, determined by the method of adiabatic compression invented by Nernst, are given, and it appears that increased oxygen concentration is accompanied by decreased temperature of ignition. A similar conclusion for methane-air mixtures may be drawn from the experiments of Taffanel and Le Floch (*Compt. rend.*, 1913, **157**, 469); so long as the ratio O_2/CH_4 was greater than, but not much less than 2·0, the ignition-temperatures of the mixtures were the same; a continued increase in the methane-concentration, however, was accompanied by a regular increase in the ignition-temperatures of the mixtures.

Using this relationship between oxygen concentration and ignition-temperature, established by Taffanel and Le Floch, we have related the ignition-temperatures of our mixtures, taking Dixon and Coward's lowest figure as being probably most nearly correct for mixtures having ratios O_2/CH_4 2·0 or more.† The temperature range between 650° for such mixtures and 715° for the

* The values employed in our calculations are: for the reaction $CH_4 + 2O_2 = 2H_2O$, Q 11,910 calories per gram; for the reaction

$$CH_4 + O_2 = CO + H_2 + H_2O,$$
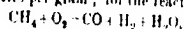
Q' ... calories per gram. For the specific heats (at constant volume) we have the following determinations:

Oxygen	0·1548	0·0000237t
Methane	0·4501	0·0000016t
Nitrogen	0·1677	0·0000016t
Carbon dioxide	0·1531	0·0000059t
Carbon monoxide	0·1730	0·0000016t
Hydrogen	2·4020	0·0000016t
Steam	0·3300	0·0001120t

† Taffanel and Le Floch, in their determinations, did not adequately allow, as did Coward, for the influence of heated surfaces.

mixture having a ratio $O_2/CH_4 = 1.20$ (the higher-limit mixture with air).

The results of the calculations are shown in Fig. 2, where q, the heat evolved, is plotted for each limit mixture against q, the heat unaccounted for or "lost." It will be seen that the two are practically proportional, the heat unaccounted for averaging for each mixture 35 per cent. of the total evolved.

This heat-loss, the magnitude of which is no doubt due to the fact that the accumulation of sufficient energy for the propagation of flame is a prolonged process—the combustion of methane taking place "by stages," * is necessarily made up of loss by (1) conduction and convection, and (2) radiation.

The number of calories transmitted by the flame to any given distant layer of unburnt gas by conduction and convection may be

FIG. 2.
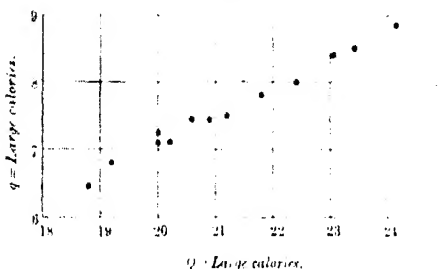
regarded as approximately proportional to the difference in temperature between the two, and a curve representing the transmission of heat by flames of different temperatures would be, as nearly as possible, a straight line.

As regards heat transmitted by flames as radiant energy, it may be it noted, has been found in the case of non-luminous coal gas flames, 30 mm. in diameter, may amount to as much as 20 per cent. of the whole heat of combustion † the effect of temperature is more difficult to estimate. Callendar suggests that Planck's equation for a single wave-length may be assumed, and for a Bunsen flame of mean wave-length $3.5\,\mu$, gives the following table of approximate values for the variation in intensity of

* The well-known "lag" in the ignition of methane is also explicable by this cause (compare T., 1911, **99**, 2020).

† Third Report, Gaseous Explosions Committee, British Association, 1913.

temperature, for comparison with the fourth power law of Stefan for the radiation of a black body:

Absolute temperature ...	1000°	1500	2000°	2500°	3000°
Radiation, Planck.	0·016	0·059	0·142	0·233	0·331
Radiation, Stefan.	0·009	0·045	0·142	0·347	0·721

Commenting on this table, Callendar says:—"The rate of variation, according to Planck's formula for a single wave-length, is much slower than the fourth-power law, and tends in the limit to be directly proportional to the absolute temperature at high temperatures. The actual rate of variation should be between these limits, but nearer to Planck, *unless carbon begins to separate in such mixtures at high temperatures*." [*]

As already noted, q, the "loss" of heat from our mixtures (in none of which did carbon separate), is practically directly proportional to Q, the total heat evolved.

EXPERIMENTAL.

The different mixtures of oxygen and nitrogen were made in large glass gas-holders holding sufficient for a dozen or more experiments, and the limit mixtures with methane prepared from them in smaller gas-holders over glycerol and water.

The method of determining the limits, and the apparatus employed, were similar to those described in our previous paper (*loc. cit.*, pp. 2020—2024). The methane used was prepared from aluminium carbide, and was purified from traces of acetylene by passing through ammoniacal cuprous chloride, and from hydrogen by passing slowly over "oxidised" palladium precipitate heated dark. It contained 99·7 per cent. of methane.

Each mixture was analysed, the methane being determined by explosion (with electrolytic gas or excess of air and oxygen added as the case might require), and the oxygen by absorption by nearly alkaline pyrogallol.

A large number of experiments with each atmosphere were made till the limits were fixed as closely as was desired. Corresponding mixtures were then carefully prepared and inflamed in a special form of explosion-vessel designed for securing a sample of "flame gases" whilst the flame was travelling (Fig. 3, p. 2592).

This explosion-vessel was a 2½-litre globe, with glass-covered electrodes reaching to the centre. Through the side of this globe are fused, in the positions shown in the photograph, two fine capillary tubes, either of which could make connexion, through a three-way tap, with a small bulb filled with mercury to within twice of its capacity. The space above the mercury in this small

[*] Third Report, Gaseous Explosions Committee, British Association, Appendix A.

Oxygen-content of atmosphere of limit mixture	Description of limit mixture	Analyses of limit mixture.			Per cent. by volume.												Calories.	
					Analysis of flame gases.						Analysis of final gases.							
		O₂	CH₄	N₂	CO₂	O₂	CO	H₂	CH₄	N₂	CO₂	O₂	CO	H₂	CH₄	N₂	Q.	q.
20·90 (air)	Higher	17·80	14·82	67·38	4·80	nil	10·10	10·50	0·85	73·75	4·99	nil	8·71	10·74	2·05	73·52	24,150	8850
19·22	"	16·74	12·93	70·33	5·00	nil	8·19	8·19	0·72	77·91	5·32	nil	7·69	7·87	1·59	77·52	23,400	8600
18·30	"	16·12	11·91	71·97	5·37	nil	7·23	7·26	0·82	79·32	5·55	nil	5·95	6·25	1·70	80·55	23,050	8400
17·00	"	15·22	10·55	74·23	5·55	nil	5·78	5·75	0·38	82·54	5·68	nil	5·68	5·20	0·56	82·82	22,400	8000
15·82	"	14·40	8·96	76·64	6·03	nil	4·19	2·93	0·25	80·62	6·43	nil	3·18	2·81	0·59	86·90	21,800	7800
14·86	"	13·59	8·36	78·05	6·27	nil	3·45	2·66	0·34	87·38	6·39	nil	2·96	2·53	0·26	87·86	21,200	7500
13·90	"	12·83	7·26	79·86	6·41	nil	1·87	1·20	0·37	90·15	6·52	nil	2·34	0·96	0·35	89·82	20,800	7450
13·45	"	12·55	6·70	80·75	6·62	nil	1·36	nil	0·55	91·32	6·92	nil	0·83	nil	0·96	91·28	20,200	7100
13·45	Lower	12·57	6·50	80·93	6·82	nil	1·31	0·35	0·35	91·17	6·03	nil	0·47	nil	0·29	92·31	20,000	7100
13·90	"	13·00	6·35	80·65	6·57	0·56	0·00	0·45	nil	91·82	7·27	0·34	nil	nil	nil	92·39	20,000	7450
14·86	"	13·05	6·15	79·90	6·46	1·54	0·48	0·18	nil	91·34	7·00	1·90	nil	nil	nil	91·10	20,000	7250
15·82	"	14·89	5·83	79·28	6·23	3·43	0·32	0·10	nil	89·92	6·60	3·65	nil	nil	nil	89·75	19,200	6800
20·90 (air)	"	19·73	5·60	74·67	6·25	9·65	0·07	nil	nil	84·03	6·30	9·58	0·05	nil	nil	84·07	18,800	6450

was thoroughly exhausted of air, and served, when the three-way tap was rapidly opened, to capture a sample of the gases at either of the two points where the capillary tubes ended within the explosion-vessel. When the whole apparatus was inverted this sample could be withdrawn, by means of a mercury pump, through the tap shown at the bottom of the photograph.

In all the limit mixtures the manner in which the flame travelled was the same. So soon as the igniting spark had been passed a cone shot up to the top of the vessel, bent over, and, after thus filling the whole of the top quarter of the globe, travelled downwards to the bottom as a uniform layer of light blue colour.* This layer had an apparent thickness of between 1½ and 2 inches, and travelled sufficiently slowly to enable the tap leading to the sampling vessel to be manipulated at the right moment.

The moment chosen for all the samples of which analyses are given in this paper was when the layer of flame had passed half-way past the end of the upper capillary tube, as indicated in fig 3 by the shading added to the photograph, which gives a very good idea of the appearance of the flame when observed through the side of the globe at the moment of sampling.

The gases were driven into the sampling-vessel under pressure of between 2 and 3 atmospheres, so that, although the space in that vessel unoccupied by mercury was under 5 c.c., between 10 and 15 c.c. of gases were obtained for analysis.

Samples of the products of combustion remaining in the explosion vessel were withdrawn for analysis after sufficient time had been allowed for complete mixture.

Results of Experiments.—The compositions of the limit mixtures, and the analyses of the " flame gases " and " final gases " are given on p. 2604.

A correction has been introduced in the analyses of flame gases as the unburned mixture contained in the capillary tube leading to the sampling-vessel.

The last two columns in the table record the calculated values of l and q plotted in Fig. 2.

These results have already been discussed in the theoretical portion of this paper. An additional point that should be noted is the preferential burning of hydrogen over carbon monoxide in all the mixtures that contain a ratio O_2/CH_4 greater than 1·5.

ESKMEALS,
CUMBERLAND.

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* In some of the higher-limit mixtures the flame had a slightly reddish tinge.

CCXLIII.—*The Propagation of Flame in Mixtures of Methane and Air. The "Uniform Movement."*

By RICHARD VERNON WHEELER.

IN the course of their well-known researches on the combustion of explosive gaseous mixtures, Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 274) studied the propagation of flame in mixtures of methane and air contained in horizontal tubes. So far as such mixtures are concerned, the general conclusions drawn by them regarding the manner in which flame is propagated were as follows.

When the mixture contained in a horizontal tube closed at one end and open at the other is ignited at the open end, the flame travels for a short distance at a uniform speed. This "uniform movement" is followed by a "vibratory movement," in the course of which the flame travels backwards and forwards in an irregular manner, the mean speed from point to point along the tube being usually greater than that of the "uniform movement." The vibrations usually continue to the end of the tube, but sometimes during a particularly violent vibration the flame may be extinguished, owing to the mixing of burnt gases with the unburnt mixture.

When the mixture is ignited at the closed end of the tube the flame travels, in short tubes at all events, with increasing speed towards the open end.

In the course of investigations on mine explosions, carried out, in the first instance, for the Mining Association of Great Britain, and, latterly, at the Home Office Experimental Station, the necessity arose for repeating Mallard and Le Chatelier's experiments regarding mixtures of methane and air.

The present paper deals with the "uniform movement," the speed of which is the normal speed of propagation of flame by conduction of heat from layer to layer of the mixture, and is constant for a given mixture at a given temperature and pressure.

Mallard and Le Chatelier made a complete study of how far the diameter, length, and material of the tubes influenced the speed and duration of the uniform movement in many gaseous mixtures, with the object of determining the limiting dimensions required to ensure that the true speed—the speed that would be attained in a mixture of indefinite extent—should be determined. Given the right dimensions of tubes, the material of which they were made did not appreciably affect the speeds. Repetition of Mallard

and Le Chatelier's experiments regarding these experimental conditions has confirmed their results.

The diameter of tube necessary to avoid cooling by the walls, and consequent retardation of the flame, was found to be greater the slower the speed of the flame. For the most slowly moving flames in mixtures of methane and air a tube of at least 5 cm. diameter is necessary. The speed of travel of flame in a tube 9 cm. in diameter is slightly greater than in a tube 5 cm. in diameter.

The duration of the uniform movement, which varies with each mixture, increases with the diameter and length of the tube up to a certain maximum, after which increase in length makes no appreciable difference. In a tube 5 cm. in diameter and 6 metres long the uniform movement in all mixtures of methane and air extends over a distance of about 150 cm., whereas in a tube of the same diameter and 2 metres long the distance travelled by the flame at a uniform speed may be less than 50 cm.

For their experiments Mallard and Le Chatelier used tubes 3 cm. in diameter and 1 metre long, and measured the speed of travel of flame over the first 50 cm. The length of the tube was insufficient to ensure that the measurements of the speed of the flame would not include part of the "vibratory movement," a fact which they themselves realised (*loc. cit.*, p. 317). Their measurements for the same mixture show, in consequence, rather wide variations. Their experiments were further vitiated by the fact that the methane used was prepared from sodium acetate ("il exhalait une forte odeur d'acetone"). Such methane ' may contain as much as 10 per cent. of nitrogen, 10 per cent. of unsaturated hydrocarbons, and 2 or 3 per cent. of hydrogen.*

The conclusions drawn by Mallard and Le Chatelier were :

(1) The speed of the uniform movement increases regularly with the percentage of methane up to a certain maximum, after which it decreases regularly. The curve obtained on plotting speeds as ordinates and percentages of methane as abscissæ is thus represented by two straight lines meeting at a point. Their curve (from Plate VIII of their paper) is reproduced in Fig. 1.

(2) The maximum speed is obtained, not with that mixture containing the quantity of methane required for complete combustion, namely, 9·4 per cent., but with a mixture containing about 12 per cent. of methane. Le Chatelier ("Leçons sur le carbone," Paris, 1908) explains this result by assuming that the speed of propagation of flame during the uniform movement depends, not only on the temperature of combustion of the mixture, but on its thermal conductivity, which is greater the greater the

* Compare Hauser, "Leçons sur le grisou." Madrid, 1908.

proportion of methane present. The thermal conductivities of air and of methane are $5·22 \times 10^{-5}$ and $6·47 \times 10^{-5}$ respectively.

Fresh determinations, made in the manner described in the experimental portion of this paper, do not bear out Mallard and Le Chatelier's results. The form of curve obtained on plotting speeds as ordinates and percentages of methane as abscissæ is shown in Fig. 1.

It will be seen that there is practically no difference between the speeds attained in mixtures containing from 9·45 to 10·55 per cent. of methane,* such differences as there are being probably within the limits of experimental error.

Near the lower- and higher-limits of inflammability, which, for horizontal propagation, are 5·4 and 14·3 per cent. respectively, the

Fig. 1.

Methane in firedamp-air mixture, per cent.
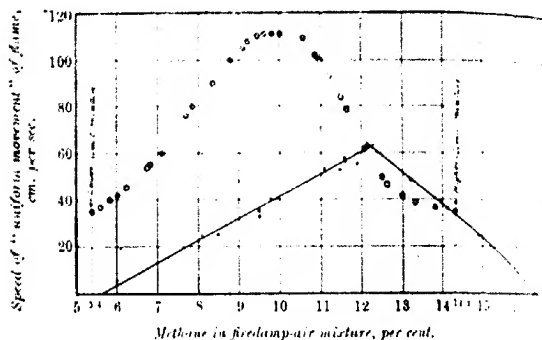
curve flattens, more noticeably towards the higher limit, and becomes, ultimately, nearly horizontal. It will be understood, therefore, that a prolongation of either "limb" of the curve, so as to cut the zero velocity ordinate, as done by Mallard and Le Chatelier to determine the theoretical limits of inflammability, is not justifiable.

Vibrations were not developed by the flames in all the mixtures. In those containing more than 12·5 or less than 5·8 per cent. of methane the flame usually travelled at a uniform or slightly decreas-

* This conclusion is confirmed by another series of experiments in which different mixtures of methane and air were ignited at the centre of a large spherical explosion vessel. The time that elapsed between the moment of ignition and the first indication of pressure on the sides of the vessel was less the higher the percentage of methane in the mixture up to 9·5 per cent. methane, after which it remained practically constant up to 11 per cent.

same speed throughout the length of the tube, although sometimes slight vibrations were noticeable in all but the "limit-mixtures." In these latter the speed of travel of flame was quite uniform throughout, and was the same for both the higher- and lower-limit mixtures.

As noted in a previous paper (this vol., p. 2593), the flame

Fig. 2.
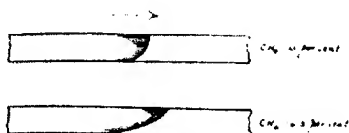
travelling horizontally in a 5·4 per cent. methane air mixture, contained in a tube 5 cm. in diameter, occupies only the upper part of the tube. The flames in the other mixtures of methane and air, including the higher-limit mixture, completely filled the cross section of the tube, the front of the flame (during the uniform

Fig. 3.
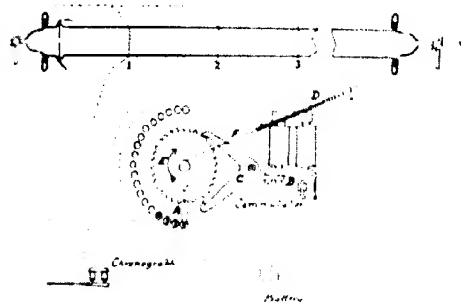
movement) being shaped as shown in Fig. 2. The faster the speed of the flame the blunter was its front.

EXPERIMENTAL.

The arrangement of glass tubes is shown in Fig. 3. Three lengths of tube of 5 cm. internal diameter, each 2 metres long, were joined together by broad pieces of stout rubber tubing, and supported horizontally in a straight line. Each end of the complete length

of 6 metres was flanged and ground to receive flanged end pieces
which were held in position by metal clips. Each end piece was
fitted with a wide-bore three-way tap. Glass-covered platinum elec-
trodes reaching to the centre of the tube, leaving a spark-gap of
3 mm., were fused 4 cm. from one end.

Another tube, similarly arranged, but of 9 cm. internal
diameter, was used for a separate series of experiments.

"Screen-wires" of copper 0·025 mm. in diameter were threaded
vertically across the tube through fine holes pierced through the
walls at certain points, the holes being afterwards covered by
adhesive plaster. In order to avoid including in the measurement
of the speed of the flame any impetus that might be given by the
igniting spark, the first screen-wire was fixed 40 cm. from the point
of ignition. Other screen-wires were fixed 50, 100, 200, 300 and
400 cm. respectively from the first.

The method of recording the time of passage of flame along the
tube was electrical. Each screen-wire carried a small electric
current, the interruption of this current when the flame melted
the wires being recorded by the movement of an electro-magnet.

It was important to avoid error due to latency or "time-lag" of
individual electromagnets. An instrument, which can be termed
an automatic commutator, was therefore designed to enable each
successive break in circuit to be recorded by the same electromagnet.
This instrument is operated in the following manner:

One terminal of the battery supplying the electric current is
connected to the brush, A, of the commutator (Fig. 3), and a lead
from the other terminal of the battery conducts the current to the
electromagnet of the chronograph, so that its armature is attracted.
The current then passes by a lead to the electromagnet on the
commutator, and that armature is also attracted; the lead carrying
the current then goes to one terminal of the screen-wires one by
explosion-tube one after the other; the other terminal of each
screen-wire is connected to the corresponding stud on the commu-
tator by separate leads.

Supposing the brush, A, to be resting on No. 1 stud (the position
that it occupies at the beginning of an experiment), the current is
then flowing through the chronograph electromagnet, the commu-
tator electromagnet, and No. 1 screen-wire; then through the
brush, A, back to the battery. Suppose now that the flame passes
along the tube and melts screen-wire No. 1; the chronograph
electromagnet releases its armature, and the pen it carries makes
a mark on the moving surface; at the same time the armature, B,
of the commutator electromagnet is released, and the anchor
escapement, C, attached to the armature, is moved. This allows the

...ed spring, D, to pull the scape-wheel, E, round by the cord, F, ...ch is wound on a drum attached to the axis of the scape-wheel. ...e brush, A, then moves on to stud No. 2, and the current at ...e begins to flow through screen-wire No. 2; the chronograph ...romagnet and the commutator electromagnet, and the arma-...s of both these are again attracted; the pen on the chrono-...ph is moved back to its former position, as also are the armature, ...and the escapement, C, whilst the brush, A, moves a little ...ther on to stud No. 2. When the flame reaches No. 2 screen-...e the same cycle is repeated and so on for as many screens as ...y be required, all the interruptions of circuit being recorded by ...one pen on the chronograph.*

...he chronograph used was the laboratory chronograph of the ...abridge Scientific Instrument Company, the speed of travel of ...moving surface (a spool of Morse paper) being recorded by a ...cond contact-clock.

Method of Conducting an Experiment. The mixtures of ...thane and air were made in a 140-litre gas-holder over water ...dered slightly alkaline by potassium hydroxide. A rapid ...rent of the mixture was passed through the explosion tube until ...gases entering and leaving had the same composition, as shown ...explosion-analyses of samples taken through the three-way taps. ...volume of mixture equal to about six times the volume of the ...e was found to be ample for sweeping out all the air contained ...the tube.

...he electrical connexions through the screen-wires and chrono-...ph having been established, the left-hand end-piece of the ...losion tube was removed (by sliding it downwards) and the ...ture ignited at the now open end by passing an induction coil ...rk.

...he methane used was a particularly pure supply of fire-damp ...m a "blower" at a colliery in South Wales, whence it was ...aned compressed in cylinders. Analysis, after removal of ...per cent. of carbon dioxide, showed it to contain 97·4 per cent. ...ethane, 2·3 per cent. of nitrogen, and 0·3 per cent. of other ...antities (carbon monoxide and ethylene). It contained no ...drogen or ethane.

...somewhat detailed description of this device has been given in the belief that ...t it is of value to other workers. The author has found it adequate for ...uring the speed of the rapidly moving flames of coal-dust explosions and coal-...st-air explosions in large galleries. Its effectiveness depends essentially on ...e rapidity with which the brush of the commutator can be made to move from ...ud to the next; by suitable proportioning and adjustment of the moving ...rts and regulation of the electric current passing through the magnets, the time ...quired for the brush to move from stud to stud can be made as little as $\frac{1}{1000}$th second.

Results of Experiments.—The results of all the determinations made of the speed of the uniform movement in different mixtures are given in the table that follows. As a general rule, the uniform movement extended for a distance of 150 cm. from the point of ignition, so that from each experiment with a particular mixture two determinations of the speed were obtained (between No. 1 and No. 2, and between No. 2 and No. 3 screen-wire respectively. Some of the more rapidly-moving flames, in mixtures containing between 9·5 and 11·0 per cent. of methane, began to vibrate just before reaching the third screen-wire; in such cases only the time between screen-wires Nos. 1 and 2 was taken as being that of the uniform movement.

Methane in fire-damp air mixture, per cent.	Speed of "uniform movement" of flame, cm. per second.
5·40	36·5, 36·0, 35·5, 35·5, 35·5, 35·5, 36·0, 35·5.
5·60	37·0, 37·0.
5·85	40, 40·5, 40·5, 40·5.
6·25	46, 46, 45·5, 45, 45·5, 45, 45·5
6·75	54, 54.
6·80	56, 55, 55, 55.
7·10	61, 59, 61, 59.
7·70	77, 77, 75, 75.
8·35	91, 90.
8·80	100, 100, 99, 100.
9·10	105, 104, 106, 104.
9·20	108, 109.
9·45	110, 110, 110, 110.
9·60	111, 111.
9·80	111, 112.
10·00	112, 110, 112, 113, 112, 110, 110, 112
10·60	109, 109, 109.
10·90	102, 102, 101.
11·00	100, 98, 99, 99.
11·20	93, 92.
11·50	84, 84, 83, 83, 85, 84.
12·10	62·5, 62.
12·50	50, 50, 49.
12·65	49, 47, 48, 46.
13·00	42·5, 42, 42, 42.
13·05	41, 40·5.
13·30	39, 38, 39, 38, 38, 38, 38.
13·80	37, 36·5.
14·30	36·0, 35·5, 35·5.

For the determinations of the speed of travel of flame in higher-limit mixture pure methane was used, since the 2·3 per cent. of nitrogen contained in the fire-damp slightly affected the high limit, whereas it had no appreciable effect on the speed of travel of flame in the other mixtures (compare this vol., p. 2595).

A similar series of determinations was made, using an explosion tube of 9 cm. internal diameter. The speeds were from 5 to 10 per second greater than those of corresponding mixtures in tube 5 cm. in diameter. The shapes of the curves connecting speed

the percentages of methane, and the limits of inflammability, were same in both series of experiments.

The propagation of flame in mixtures of methane and air, and mixtures to which nitrogen has been added, has been further tried. An account of the work will be communicated later to the Society.

Addendum.

Since this paper was prepared an account has appeared of experiments on the same subject by A. Parker and A. V. Rhead (this p. 2150). It is surprising to find that these authors are apparently unacquainted with Mallard and Le Chatelier's complete researches dealing with the "uniform" and "vibratory" movements during the propagation of flame in gaseous mixtures contained in glass tubes, as outlined in the present paper. Their results are interesting in that they emphasise the necessity, pointed out by Mallard and Le Chatelier, of employing tubes of ample diameter when conducting experiments of this nature; the tubes they used were of too small a diameter to enable them to determine either the true character of the speed-percentage curve or the limits of inflammability.

CHEMICALS,
CUMBERLAND.

CXLIV.—*Volatile Oil from the Leaves of* Barosma venusta.

By ERNEST GOULDING and OSWALD DIGBY ROBERTS.

The genus *Barosma*, of which about thirty species exist in South Africa, derives its chief importance from the fact that certain species yield the so-called Buchu leaves, which are employed in medicine as mild disinfectants of the urinary tract. The physiological activity of the leaves is principally due to the volatile oil which they contain. The source of Buchu leaves of the British Pharmacopœia, or "short Buchu," is *Barosma betulina*, Bartl. and Wendl., but the leaves of *B. crenulata*, Hook. and *B. serratifolia*, Willd., are also met with in commerce under the name of "long Buchu."

Another species of Barosma, *B. venusta*, Eckl. and Zeyh., occurs in considerable quantities in the Uitenhage District of the Cape Province. Information was desired in South Africa as to the possible value of the leaves of this plant in comparison with Buchu

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leaves, and an examination of the material was therefore undertaken at the Imperial Institute.

The most characteristic constituent of the oil of *Barosma betulina* is diosphenol, which is present in quantities of 20—30 per cent; the oils of *B. crenulata* and *B. serratifolia*, however, contain only very small proportion of this substance. The results of the present investigation show that the oil of *B. venusta* differs very considerably in odour and composition from that of Buchu leaves in that it does not contain any diosphenol.

In 1911 a sample of the leaves of *Barosma venusta* was received at the Imperial Institute from the Cape Province, South Africa. On distillation in a current of steam it yielded 2·7 per cent. of volatile oil, which was of a lemon-yellow colour and pleasant odour, and had D^{15} 0·877 and a_D^{20} 1°4′ in a 100-mm. tube.

A larger consignment of the leaves, forwarded in 1913 furnished 2·0 per cent. of volatile oil with the following constants:

D^{15} .... 0·865
a_D^{20} in 100 mm. tube .... + 0·47′
Acid value .... 5·6
Ester value .... 6·2

(Corresponding with 2·2 per cent. of esters, calculated as $C_{10}H_{17}·OAc$.)

Ester value after acetylation 55

(Corresponding with 15·7 per cent. of total alcohols, or 14·3 per cent. of free alcohols and 2·2 per cent. of esters.)

Fractional Distillation of the Oil.

On distilling the oil under atmospheric pressure the following fractions were obtained, but some decomposition occurred:

Fraction.	Per cent.	Boiling point.	D^{15}.	a_D in 100 mm. tube.
I.	44	163—190°	0·8100	inactive
II.	17	190—205	0·8932	inactive.
III.	28	205—230	0·9531	+ 0·30′
IV.	9	230—245	0·9610	liquid becomes coloured towards end of this determination.
Residue	2	—	—	

Isolation and Identification of Myrcene.

When a portion of the oil was distilled under 60 mm. pressure, about 48 per cent. collected between 83° and 88°. This liquid, after being treated repeatedly with sodium and redistilled, had D^{15} 0·8060, and was optically inactive; it distilled at 165° under atmospheric pressure, but suffered partial decomposition

The hydrocarbon exhibited the properties characteristic of myrcene, for which the following constants have been recorded:

Power and Klober [1]	D^{14} 0·8023	b. p. 167°.
Semmler [2]	—	b. p. 171—172°.
Chapman [3]	D^{15} 0·8046	b. p. 166—168°.
Enklaar [4]	D^{15} 0·8013	b. p. 166—168°.
Semmler and Mayer [5]	D^{20} 0·7937	

Pharm. Zentralh., 1895, **13**, 61.

T, 1903, **83**, 507.

[3] Ber., 1911, **44**, 2010.

[2] Ber., 1901, **34**, 3216.

[4] Diss., Utrecht, 1905.

The terpene showed a great tendency to resinify, and readily combined with four atoms of bromine. On reduction with sodium and alcohol it was converted into a compound having D^{15} 0·7860, a value which agrees well with those recorded for dihydromyrcene, namely, 0·7802 and 0·7852, by Semmler (*loc. cit.*) and Enklaar (*loc. cit.*) respectively. This reduction product furnished a tetrabromide, melting at 91°, which crystallised from methyl alcohol in long, white needles. The melting point of dihydromyrcene tetrabromide has been given as 87° by Semmler and Mayer (*loc. cit.*) and 88° by Enklaar (*loc. cit.*). By the action of a mixture of glacial acetic acid and sulphuric acid on the original terpene, an acetate was obtained which resembled linalyl acetate in odour, and, on hydrolysis, yielded an alcohol. This alcohol, when oxidised with chromic acid, did not furnish citral, but the odour of the product suggested the presence of some other aldehyde. These observations accord with those of Barbier (*Compt. rend.*, 1901, **132**, 1048) on the oxidation of myrcenol. The existence of myrcene in the oil is therefore established.

Aldehydes · Identification of Anisaldehyde.

A portion of the oil was shaken with solution of sodium hydrogen sulphite. After the aqueous liquid had been separated and washed with ether, it was rendered alkaline by the addition of sodium peroxide, and extracted by repeated agitation with ether. The ethereal solution was dried with anhydrous sodium sulphate, and the ether was removed by distillation. The residue, amounting to about 0·5 per cent. of the original oil, appeared from its taste and odour to consist chiefly of anisaldehyde, and, on oxidation with potassium permanganate, was readily converted into anisic acid, which after recrystallisation melted at 183—184° (anisic acid has b. p. 184°).

Alcohols: Indication of the Presence of Linalool.

The fraction boiling at 190—205° under atmospheric pressure consisted largely of alcohols, and had a sweet odour resembling that of linalool; on oxidation it yielded citral, which was characterised by its odour and by the preparation of α-citryl-β-naphtho-cinchoninic acid, melting at 199°. It is therefore probable that the alcohols consist in part of linalool.

Phenols: Absence of Diosphenol.

When the original oil, after being washed successively with sodium carbonate solution and sodium hydrogen sulphite solution to remove acids and aldehydes, was treated with 5 per cent. solution of sodium hydroxide, an absorption amounting to only 0·2 per cent. took place. On acidifying the solution and extracting with ether, a phenolic substance was obtained, but in too small a quantity to admit of investigation; this product did not give any distinctive coloration with ferric chloride. No evidence could be obtained of the presence of diosphenol.

Ethers: Identification of Methylchavicol.

A fraction of the oil, boiling at 213—218°, was found to consist of methylchavicol, which was identified in the following way.

The fraction was heated with 20 per cent. alcoholic potassium hydroxide solution for two days in a sealed tube at 200°. The contents of the tube were diluted with water and extracted with ether. After drying the ethereal solution with anhydrous sodium sulphate, and removing the ether by evaporation, it was found that the oil had been converted almost quantitatively into anethole, which boiled at 232—234°, and solidified on cooling to a mass of crystals, melting at 22°. The product possessed the odour and sweet taste characteristic of anethole. Determinations of methoxyl in the original oil gave results indicating the presence of this per cent. of methyl ethers (calculated as methylchavicol):

0·2770 gave 0·0947 AgI. OMe = 4·51 or $C_9H_9 \cdot OMe = 21·5$ per cent.
0·2895 „ 0·0980 AgI. OMe = 4·46 „ $C_9H_9 \cdot OMe = 21·3$ „ „

Constituents of High Boiling Point.

The fraction which distilled at 230—245° was brownish-yellow, viscous, and had a somewhat empyreumatic odour; it probably contained sesquiterpenes, together with polymerides and decomposition products of myrcene, due to the high temperature to which it had been heated.

Summary of Results.

The results of this investigation indicate that the volatile oil of *Leucas cenusia* leaves has approximately the following composition:

	Per cent.
Hydrocarbons, chiefly or entirely myrcene	43·0
Aldehydes, " " " anisaldehyde	0·5
Phenols	0·2
Phenol ethers, methylchavicol	21·4
Alcohols, partly linalool (calculated as $C_{10}H_{17}\cdot OH$)	14·3
Esters (calculated as $C_{10}H_{17}\cdot OAc$)	2·2
Sesquiterpenes, loss, etc. (by difference)	18·4

In conclusion, reference may be made to an examination of this oil by Jensen (*Pharm. J.*, 1913, [iv], **36**, 60). Although the trees from which he distilled the oil were obtained from the same source as those used in the present investigation, the results show certain differences, of which the most remarkable is that he found 6 per cent. of chavicol, whereas the authors have not been able to detect the presence of even a trace of this phenol.

XLV. —Sodium Amalgams: Specific Volumes and Electrical Conductivities.

By ERNEST VANSTONE.

account has already been given of the investigation of the thermal diagram and the determination of the specific volumes of solid and liquid sodium amalgams (*Trans. Faraday Soc.*, 1911, **7**,

it was shown that when specific volume was plotted against concentration of amalgam expressed in atomic percentages, smooth curves were obtained, although the corresponding thermal diagram showed many discontinuities.

Since the publication of the first paper, the specific volumes have been plotted against concentrations expressed in percentages by weight. It was shown by Maey (*Zeitsch. physikal. Chem.*, 1899,

29, 119) that the specific volume of alloys is a linear function of the concentration expressed in percentages by weight. Hence the new volume-concentration diagram (Fig. 1) consists of a series of straight lines, having nearly the same obliquity, and confirms the existence of inter-metallic compounds shown by the thermal diagram.

The concentrations (in atomic percentages of sodium) where the

FIG. 1.
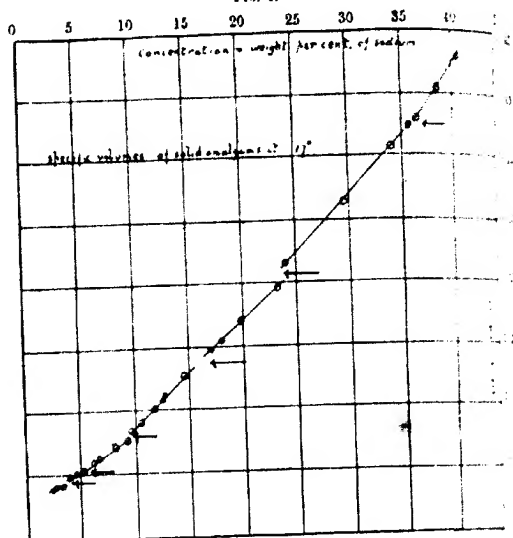
discontinuities occur are given below; those obtained by the thermal method are given for comparison.

Concentrations.

Weight per cent.	Atoms per cent.	Atoms per cent. (thermal)
36·0	83·0	85·2 and 87·4
23·8	73·5	73·5
16·4	63·0	63·3
9·4	47·5	47·5 and 51·5
5·2	32·5	33·3
2·8	20·0	17·9

When the comparative slope of the lines in Fig. 1 is considered, and the fact that the concentrations have to be read from the diagram in percentages by weight and then transferred

mass percentages, the agreement between columns (2) and (3) in the above table is as satisfactory as can be expected.

The Constitution of Liquid Amalgams.

Many researches have been carried out on liquid amalgams, having for their object the determination of the molecular complexity of metals in amalgams rich in mercury.

Measurements of (1) vapour pressure, (2) E.M.F., and (3) lowering of freezing point show that the metal is present as a single atom, yet they cannot prove that that atom is not combined with a certain number of atoms of mercury.

Two other researches may be mentioned. (1) The rates of diffusion of metals in mercury have been found, and when atomic diffusivities are plotted against atomic weights, two curves are obtained; metals which do not form compounds with mercury are higher diffusivities and lie on one curve, whereas metals which are known to form compounds lie on a second curve with lower diffusivities. It has been suggested that compounds MHg_n are formed in which the attached mercury retards the process of diffusion.

(2) Bornemann and Müller (_Metallurgie_, 1910, **7**, 396) determined the electrical conductivity of liquid sodium amalgams, and obtained a marked discontinuity at a concentration of 33·3 atoms per cent. of sodium, showing the existence of the compound $NaHg_2$ in the liquid condition.

The thermal diagram indicates the existence of at least five other compounds of sodium and mercury, but their existence in the liquid condition was not made manifest by the electrical conductivity experiments.

We are led to inquire why this is so. Bornemann and Müller's experiments were carried out at very high temperatures, and it is possible that all the other intermetallic compounds were dissociated, the compound $NaHg_2$ was stable, since it has a much higher melting point, namely, 360°, than the other compounds; it is at the maximum point on the thermal diagram; other compounds, with the possible exception of Na_3Hg, do not show maxima.

It was thought that indications of the existence of the other intermetallic sodium mercury compounds might be obtained if physical properties were investigated at temperatures not far removed from the melting points of the alloys.

The specific volumes of liquid alloys at 110°, 184°, and 237° have already been determined.

The concentration-volume diagram for 110° is shown in Fig. 2.

It is seen that the specific volume of the liquid alloys is a ___
function of the concentration when expressed in percentage of
weight.

The absence of discontinuities shows that the intermetallic com-
pound Na$_2$Hg does not exist at 110°.

A consideration of Fig. 1 shows that the property of volume
does not suffer any profound change when combination takes
place between the metals sodium and mercury, so further investi-

FIG. 2.
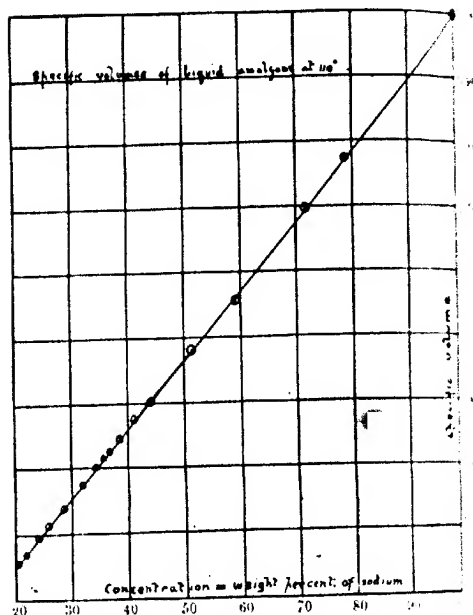
gations were made by means of electrical conductivity measure-
ments of liquid amalgams.

The Electrical Conductivities of Liquid Amalgams

The method of experiment has already been described in a former
paper. The amalgams were kept under paraffin, and drawn
into a capillary spiral having platinum terminals sealed into
glass at convenient points.

The spiral was open at the lower end and fitted with a glass ？ at the top. It was connected to a hydrogen apparatus, and ？？ allowing any amalgam to enter, it was dried and filled with ？ hydrogen.

The capillary was 1 mm. in diameter, and the distance between ？ platinum terminals about a metre when unwound. It was ？？？ by finding the resistance of mercury filling the spiral.

Fig. 3
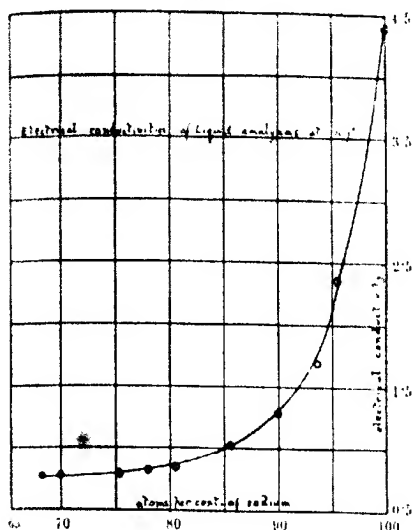
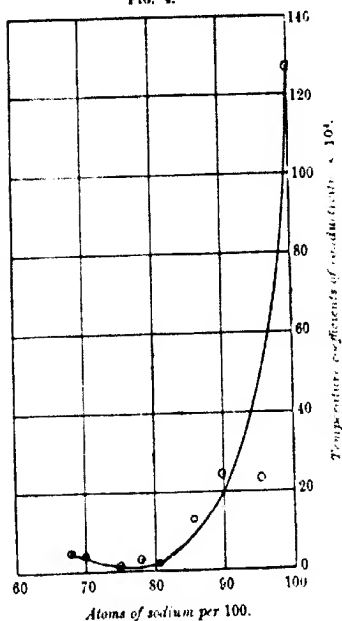Temperatures of approximately 110° and 135° were obtained by ？？？ with boiling toluene and xylene.

？？ results are given in the table below; concentrations are ？？？ in atomic percentages of sodium; the resistances refer ？ spiral in which the resistance of mercury at 17° is 1 ohm.

It will be noticed that conductivity measurements have been ？？ for each alloy at two temperatures differing by 26°. The ？？ for the temperature-coefficient has thus been obtained.

Electrical Conductivities of Liquid Amalgams.

Concentration.	Resistance at 107°.	Conductivity.	Resistance (133°).	Conductivity.	Temperature coefficient.
100	0·2285 0·2286 0·2266 0·2260	4·397	0·2455 0·2449 0·2477	4·065	0·0274
95·36	0·4225	2·366	0·4334	2·307	0·0233
93·54	0·5835	1·714	—	—	—
89·88	0·7749	1·2905	0·8139	1·2286	0·0428
85·60	0·9796	1·0208	1·0133	0·9868	0·0426
80·50	1·1569	0·8643	1·1627	0·8600	0·0516
77·89	1·2124	0·8248	1·2248	0·8164	0·0342
75·31	1·2532	0·7979	1·2584	0·7946	0·0373
71·74	—	—	1·3087	0·7641	
70·02	1·2921	0·7739	1·3096	0·7635	0·0480
68·08	1·2968	0·7711	1·3208	0·7571	0·0865

Fig. 4.

Atoms of sodium per 100.

The conductivity-concentration curve for 107° is shown in Fig.
It is a rectangular hyperbola possessing no discontinuity
results for 135° form a similar curve, which would be
below that in Fig. 3.

It will be observed that the fall in conductivity is most marked at 100 to 85 atoms per cent. of sodium, the conductivity at per cent. being less than one-fourth the value for pure sodium. It may be pointed out that the concentration of 85 per cent. is at the eutectic point in the thermal diagram.

The differences in conductivity for a temperature range of 26° are small, and become much smaller as the mercury content of the alloys increases.

The temperature-coefficient falls with extreme rapidity as we go from pure sodium to alloys containing 5 and 10 atoms per cent. of mercury. The coefficient has an extremely small, almost constant value for alloys containing more than 20 atoms per cent. mercury. This is shown in Fig. 4. The curve does not give any indication of the formation of compounds.

The conclusion to be drawn from electrical conductivity measurements for liquid amalgams is thus the same as from specific volume determinations, namely, that the intermetallic compounds of sodium and mercury are completely dissociated in the liquid solution.

It is possible also from the present and from previous work to compare the relative values of the properties specific volume, electrical conductivity, and freezing point in determining the constitution of alloys, and it is quite evident that the last is far superior in the certainty of its indications.

THE TRAINING COLLEGE,
    CAERLEON,
    MONMOUTHSHIRE.

CCXLVI.—*The System Ethyl Ether Water Potassium Iodide–Mercuric Iodide. Part III. Solutions Unsaturated with Respect to Solid Phases in the Four-component System.*

By ALFRED CHARLES DUNNINGHAM.

The fact that the surface of saturation with respect to solid phases cuts the tetrahedron into two parts has been used as an arbitrary reason in the consideration of the system. That part representing unsaturated solutions, or complexes of solid and solution, has partly been considered (this vol., p. 724, *et seq.*). The other represents liquid phases only, and extends from the surfaces of

saturation with respect to solid to the edge BC of the tetrahedron (Fig. 11, Part II). It is therefore bounded by the solid surfaces and portions of the side-planes, namely, $BFGHJZ$ on $Cabefmgde$ on ACD, $BPNMaC$ on ABC, and $BZQPeC$ on B, has been found experimentally that liquid mixtures saturated with solid phases can exist as one, two, or three layers respectively.
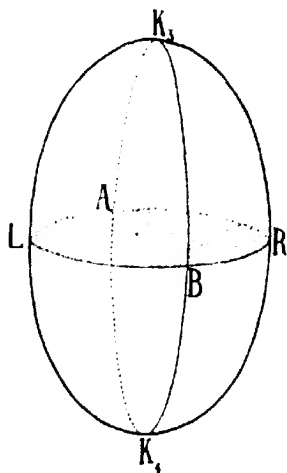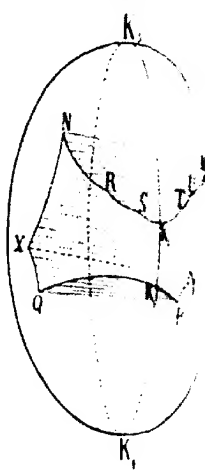

Fig. 13.   Fig. 14.

The above space representing liquids only is therefore divided in at least three parts, corresponding with these three cases.

The Formation of Two Liquid Layers.

It will be well to consider first the conditions under which mixtures, unsaturated with solid phases, can exist as two In a four-component system all such mixtures lie inside what be called a " two liquid volume," whilst the layers themselves given by points on the surface enclosing this volume. A liquid volume," if complete, is more or less egg-shaped, and circled by a critical curve, AK_3BK_4, as shown in Fig. 13. critical curve divides the binodal surface into two parts, any solution a on one part is conjugate with a definite solution

* For Fig. 12, see this vol., p. 731.

the other part. The line ab, which lies entirely inside the two
and space, represents all mixtures of a and b.

A "two-liquid volume" may be intersected by the side-planes
the tetrahedron, or by the solid saturation surfaces of the system,
that part of it becomes metastable. In Fig. 13 $LARB$ represents
a curve of intersection, so that either the upper or lower
part of the two-liquid space is rendered metastable. ALB and
RB are conjugate curves, that is, solutions given by points on
LB are in equilibrium with definite solutions given by points on
RB. That this must be so will be seen at once from the following
considerations. When $LARB$ is the curve of intersection of a side-
plane with the binodal surface, it lies entirely in that side-plane,
and represents a three-component system. If solutions on ALB
are not in equilibrium with solutions on ARB, they would there
be conjugate with solutions given by points somewhere else
the right-hand side of the binodal surface; that is, either inside
outside the tetrahedron. In the former case a solution on ALB
a three-component system would be in equilibrium with a
solution in a four-component system, in the latter with a non-
existent solution. Neither of these cases is possible. In a similar
it can be shown that when the binodal surface is intersected
by a solid saturation surface, ALB and ARB are conjugate, for if
they were not, a saturated solution would be in equilibrium with
either an unsaturated or a supersaturated solution. When,
however, the binodal surface is intersected by a plane such as ALD
Fig. 11 (Part II), ALB and ARB are not necessarily conjugate.
In Fig. 11 (Part II) $NRSK_1TUM$ and QK_2P are curves of inter-
section of a binodal surface and the solid saturation surfaces, whilst
N and MY, QX and PY are curves of intersection of the binodal
surface and the side-planes. $XNRSK_1TUMYPK_2QZ$ therefore
represents the boundary of the stable portion of the binodal
surface, K_1 and K_2 being points on the critical curve, the stable
part of which therefore extends from K_1 to K_2.

The relation between the stable and metastable portions of the
two-liquid space is shown in Fig. 14, which is lettered to correspond
to Fig. 11. The critical curve K_1K_2 divides the stable portion of
the binodal surface into two parts, $NRSK_1K_2QX$ and

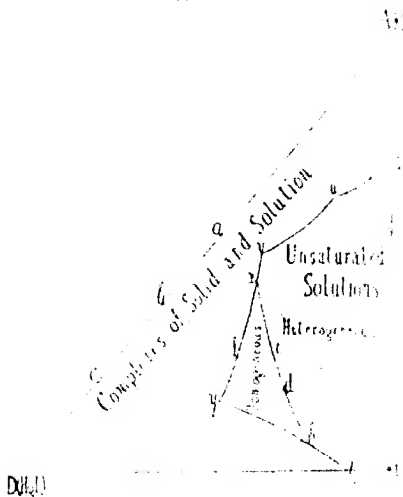$$MUTK_1K_2PY,$$

so that all solutions given by points on one part are conjugate
to solutions given by definite points on the other part. When,
therefore, all pairs of conjugate points on $NRSK_1K_2QX$ and
UTK_2K_2PY are joined, a space is formed, inside which lie all
the mixtures existing as two layers. This space is bounded by
the stable portion of the binodal surface, $XNRSK_1TUMYPK_2QZ$,

and the surfaces formed by joining all pairs of conjugate points on the following pairs of lines: K_2Q and K_2P, QX and PY and YM, NR and MU, RS and UT, SK_1 and TK_1. Outside this space lie unsaturated homogeneous liquids, so that the closed binodal surface divides the unsaturated space into two parts, one of which represents liquid mixtures existing as two layers, the other homogeneous liquids. The latter is bounded by the following surfaces (see Fig. 11, Part II):

(1) The binodal zurface $XNRSK_1TUMYPK_2QZ$.

Fig. 15.

(2) The saturation surfaces $FNRG$, $MabU$, $GRSH$, $Hbcde$, HSK_1TuJ, $ZJwpnmgdePK_2Q$.

(3) The portions of the side-planes $BFGHJZ$ and $Cabefmgde$ on ACD, $BFNX$ and $CaMY$ on ABC, and $ZQXP$ and $CDef$ on BDC.

The conjugate curves cp and fn, cd and fg, gn and dp appear to be intersections of saturation surfaces and side-planes with a second binodal volume which extends into the tetrahedron, and, as will be shown later, intersects the binodal volume, of which

$$NRSK_1TUMYPK_2QX$$

is the stable part of the surface.

As in the case of solutions saturated with solid phases, the

occurring in the system are best understood by studying the sections of a series of planes with the binodal and saturation surfaces. Fig. 15 shows diagrammatically the curves of intersection with a plane as ADL in Fig. 11. As in Fig. 12 (Part II), $xyhk$ is the curve of intersection of the solid saturation surfaces, x and h lying on the critical curves SK_1T and QK_2T' respectively. The intersection of the plane with the stable binodal surface thereon extends from x to h, as shown by the curve xdh in Fig. 15. In this figure it is assumed that L represents a mixture of ether and water in which neither component is present in sufficient proportion to cause complete miscibility. $qxyhkL$ represents liquid mixtures. Those lying on $xdhy$ are homogeneous; those $qxzdhkL$ exist as two layers. If L is joined to x and h, and Lh are produced to meet AD in a and c respectively, the AD, which represents mixtures of potassium and mercuric iodides, is divided into three parts. Points on Aa and cD represent mixtures which on addition to L cause saturation without homogeneity. Mixtures on ac, however, on addition to L cause the liquid to become homogeneous before saturation is reached; for example, on adding the solid mixture b to the liquid L, the mixture follows the line Lb. From L to d it exists as two layers; at d it becomes homogeneous, and then follows df until saturation is reached at f. The solid phase is necessarily potassium mercuric iodide, mercuric iodide, or, if Lb passes through y, a mixture of the two.

The position of L on BC (Fig. 11) determines the positions of x and y on the curves SK_1T and QK_2T' respectively. In most cases the plane ADL cuts the critical curve K_1K_2 in a point e; xe and eh are on opposite sides of this critical curve. When, therefore, Lb cuts xe, which represents upper or ethereal layers, the mixture comes homogeneous by the disappearance of the lower layer and persistence of the upper. When it cuts eh (as in Fig. 15), which represents lower or aqueous layers, homogeneity ensues by the disappearance of the upper layer and persistence of the lower. When Lb passes through e, the two layers become identical. The curve xdh can lie entirely on one or other of the binodal surfaces without intersecting the critical curve. When it lies entirely on the part representing upper or ethereal layers, all mixtures become homogeneous by the disappearance of the lower layer; similarly, when it lies entirely on the part representing lower or aqueous layers, all mixtures become homogeneous by the disappearance of the upper layer.

The Formation of Three Liquid Layers.

In a ternary system three liquid layers, unsaturated with regard to solid phases, arise through the intersection of three binodal curves (see Roozeboom, "Die Heterogene Gleichgewichte," In Part 2). In a quaternary system the three layers arise through the intersection of three "two-liquid volumes." Fig. 16 shows the simplest case of this, where three liquid layers occur in the two ternary systems ACB and ADB. Thus, in the system ACB, aK_1b, bK_1c, cK_2a are the stable portions of three binodal curves intersecting in a, b, and c. These points of intersection represent the
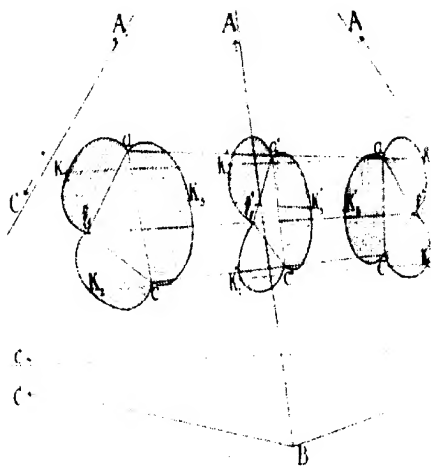
three conjugate liquids, the composition of which cannot vary in the ternary system; similarly, in the system ADB, $a'K_2'b'$, $b'K_3'c'$, $c'K_3'A'$ are the stable portions of the binodal curves, a', b', and c' the three conjugate liquids. We have already seen that a binodal curve in a ternary system may be considered as arising from the intersection of the side-plane representing the ternary system with the surface of a "two-liquid volume" in the quaternary system. It therefore follows that between each pair of binodal curves in the ternary systems ACB and ADB a binodal surface extends right through the four-component system. There are thus three binodal surfaces intersecting along the lines aa', bb', and cc'. These are

present series of three conjugate liquids, such that a solution
represented by a point a'' on the line aa' is in equilibrium with
solutions represented by definite points b'' and c'' on the lines bb'
and cc' respectively. $a''K_2''c''K_1''b''K_2'''$ is a section across the
space enclosed by the three binodal surfaces, such that a'', b'', and
are conjugate points. $a''K_2''b''$, $b''K_1''c''$, and $c''K_2'''a''$ are thus
liquid areas, whilst $a''b''c''$ is a three-liquid area. Any point
this triangle represents a mixture of the three liquids a'', b'', and
The position of the point shows the relative amounts in which
are present.

From the consideration of a series of such sections it is clear
the volume enclosed by the three intersecting surfaces is
divided into four parts, namely, three two-liquid volumes and a
three-liquid volume, lying inside the others, of which $a''b''c''$ is a
face.

In the system under consideration three liquid layers do not

Fig. 17.
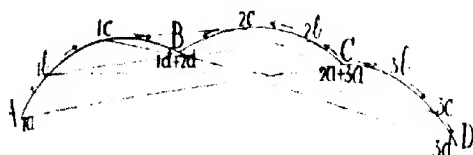
AB *represents bottom layers.* BC *represents middle layers.*
CD *represents top layers.*

in any of the ternary systems. The three-liquid volume
therefore lies entirely inside the tetrahedron. The three curves
representing a series of three conjugate liquids have been deter-
mined experimentally, and their form is shown graphically in
17, the same projection being employed as in Fig. 11 (Part II).
numbers obtained are given in table VI.*

In connexion with the experimental work involved in the three-liquid
equations, one point is of particular interest. It was found that three stable
layers could be obtained easily when freshly purified ether was used, but that
ether which has been kept some time, and liberated traces of iodine from
the iodide solution, caused a curious form of metastability, which is best
studied by the following experiments. A liquid mixture was prepared contain-
ing 245 grams of potassium iodide, 11·067 grams of mercuric iodide, 9·447 grams
water, and 19·440 grams of freshly purified ether. This gave three liquid layers
were perfectly stable at 20°. The same mixture, in the preparation of which
very "pure" ether was used, gave only two stable layers at 20°. It was found
able, however, to prepare three metastable layers by gradually warming the
two without agitation. Thus, the mixture existed as two stable layers at 10°,

TABLE VI.

The System: Ethyl Ether–Water Potassium Iodide Mercuric Iodide at 20°.

Three liquid layers with no solid phase

| No. | Percentage composition of top layer. | | | | Percentage composition of middle layer. | | | | Percentage composition of bottom layer. | | |
	KI.	HgI$_2$	Et$_2$O.	H$_2$O.	KI.	HgI$_2$	Et$_2$O	H$_2$O.	KI.	H$_2$O	HgI$_2$
*57	2·1	6·2	88·3	3·4	16·7	30·8	23·4	29·1	16·7	30·4	
†58	2·2	6·2	87·9	3·7	16·6	30·9	23·2	29·3	—		
59	2·2	6·8	87·0	4·0	15·8	30·6	28·5	25·1	18·5	32·4	
†60	2·3	6·8	86·7	4·2	14·3	29·4	33·3	23·0	—		
‡61	—	—	—	—	13·2	30·1	37·7	19·0	20·3	33·0	12·5
62	2·7	7·7	85·4	4·2	13·1	28·7	38·7	19·5	20·5	32·9	12·5
63	2·7	7·5	85·4	4·4	12·5	28·8	39·4	19·3	20·8	32·6	12·5
64	4·1	12·8	77·5	5·6	10·3	26·6	47·7	15·4	21·9	34·2	12·4
65	4·5	11·2	78·2	6·1	10·3	25·9	49·1	14·7	22·2	34·5	19·7
66	5·8	16·6	68·9	8·7	8·8	21·9	58·0	11·3	22·4	35·9	16·1
67	6·0	16·8	69·2	8·0	8·7	21·6	58·6	11·1	23·0	34·7	
§68	7·1	19·2	64·3	9·4	7·1	19·2	64·3	9·1	22·4	35·2	16·8

* In No. 57, the middle and bottom layers are identical, that is, two critical solution.

† Nos. 58 and 60 give the solutions left when the bottom layer disappeared.

‡ No. 61 gives the solutions left when the top layer just disappears.

§ In No. 68, the top and middle layers are identical, that is, two critical solution.

Any solution represented by a point on AB is in equilibrium solutions represented by points on BC and CD respectively represents bottom, BC middle, and CD top layers. One

but gave rise to three layers when placed in the thermostat without agitation. On shaking, however, the three layers, which were cloudy immediately gave only two stable layers. It was further found that the amounts of the three metastable layers depended on the amount that temperature was raised without agitation. The same phenomena was observed whenever a three-liquid mixture was prepared with ether which had been freshly purified.

It has not been found possible to investigate the matter further and the nature of the action of impure ether on the equilibrium existing between the layers is still in doubt. The effects observed, however, were that the traces of impurity amounting to an almost negligible percentage of the mixture, and it appears probable that these traces of impurity affected the tension existing between two of the layers (the upper two in all cases) to an to such an extent as to render equilibrium between them impossible.

The ether used in the determinations was purified as follows: It was washed with dilute permanganate solution, slightly acidified with sulphuric acid, until permanganate was no longer decolorised. It was then distilled and over anhydrous sodium carbonate for some days, when it was again washed. third distillation over anhydrous sodium carbonate completed the purification; the final product never produced metastability between three liquid layers.

tions are lettered alike; thus $1b$, $2b$, and $3b$ are in equilibrium
with one another. A and C represent two conjugate liquids, such
that when A (the lower layer) moves along AB, C (the upper layer)
rise to two layers, which move along CB and CD respectively,
as shown by the arrows. When the top layer (No. 3) reaches D,

Fig. 18.
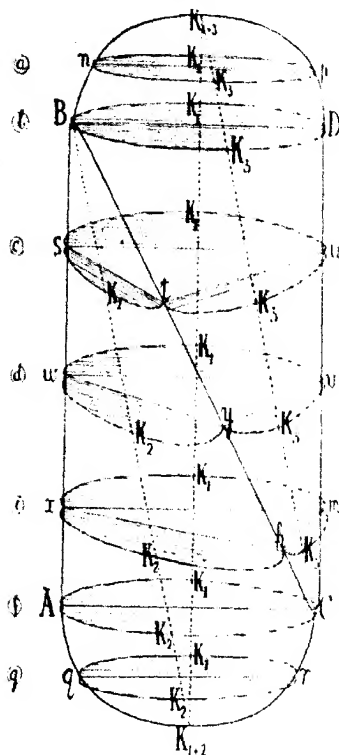
the bottom (No. 1) and middle (No. 2) layers both reach B, where
become identical, thus leaving only two layers, B and D, in
equilibrium. This reaction is reversible. Starting with B and D,
D, the upper layer, moves along DC, B, the lower layer, gives
to two layers which move along BA and BC respectively.

When the bottom layer (No. 1) reaches A, the middle (No. ?) top (No. 3) layers reach C, and become identical, leaving A and C in equilibrium. The changes may be represented thus

$$L_A + L_C \longrightarrow L_1 + \underbrace{L_2 + L_3}_{C} \longrightarrow \underbrace{L_1 + L_2}_{B} + L_3 \longrightarrow L_1 + L_?$$

and

$$L_B + L_D \longrightarrow \underbrace{L_1 + L_2}_{B} + L_3 \longrightarrow L_1 + \underbrace{L_2 + L_3}_{C} \longrightarrow L_1 + L_?$$
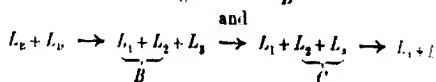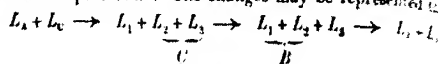
FIG. 19
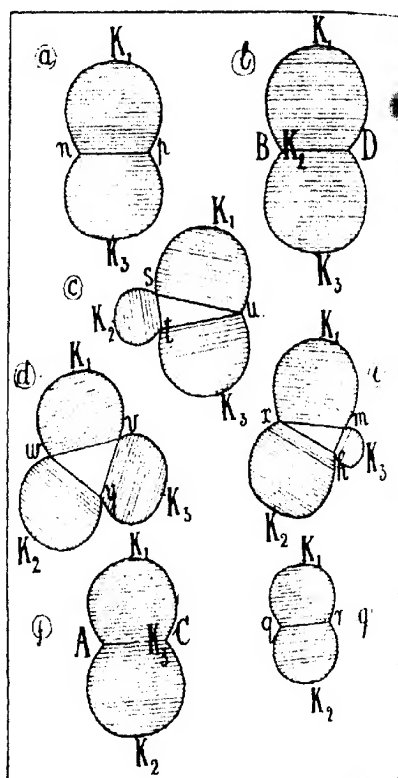
Fig. 18 shows a type of equilibrium in which the intersec... three binodal surfaces gives rise to three-liquid curves simil...

shown in **Fig. 17.** The three surfaces, the critical curves of
are lettered K_1, K_2, and K_3 respectively, intersect along AB,
and CD, which are lettered to correspond with Fig. 17. The
diagram is best understood by studying a series of sections
of the figure, which are shown in detail in Figs. 19a, 19b, 19c,
19e, 19f, and 19g. With regard to these, the following points

FIG. 20.
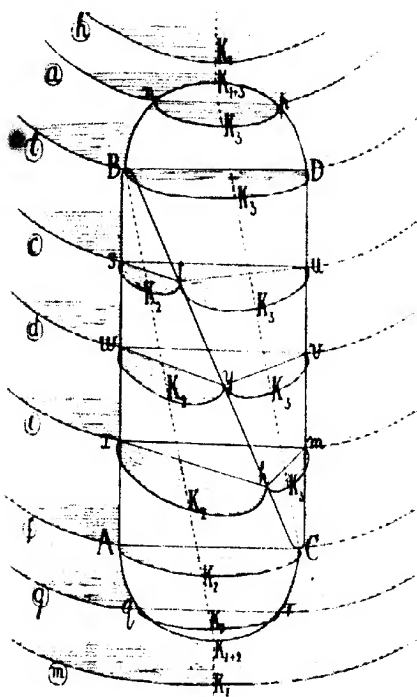
mentioned. In Fig. 18 $BK_{1\cdot3}D$ is the curve of intersection
of binodal surfaces, the critical curves of which meet at $K_{1\cdot3}$,
it is a section of the space enclosed by these two surfaces.
A point on nK_1pK_3 represents a mixture of two conjugate
Points on nK_1p represent mixtures of liquids on nK_1 and
respectively, lying on binodal surface 1, whilst those on nK_3p
represent mixtures of liquids on nK_3 and pK_3 respectively, lying

on binodal surface 3. Section (b) differs from (a) in that E ....
critical solution, from which arise liquids s and t of .....
Sections c, d, and e show three-liquid areas, namely, s... ...
shm respectively. In section (f) C is a critical solu... ....

Fig. 21.
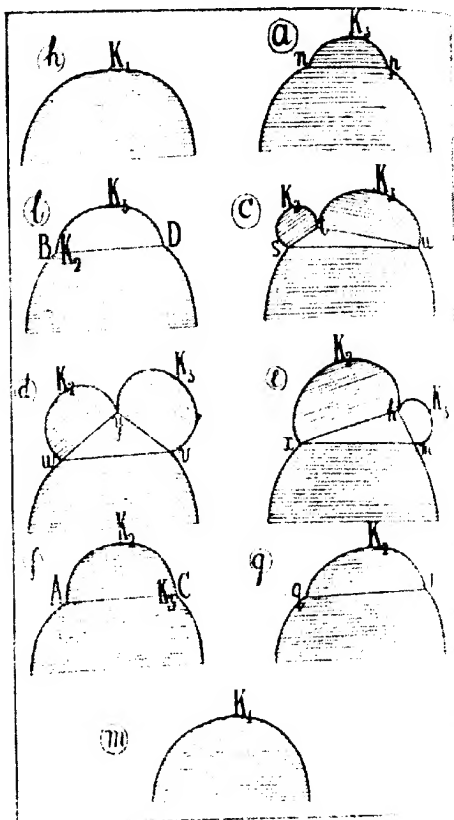
from w and h of (c), which have become identical. (c) ....
as (a), with the difference that binodal surface 3 has been .....
by binodal surface 2. The three-liquid volume terminates in
lines BD and AC, and its general form is clear from ....
(d), and (e).

In the system under consideration two of the intersecting "two-liquid volumes" are also intersected by side-planes of the tetrahedron or by solid saturation surfaces. The curves formed by these intersections have already been considered. There is no indication that the third "two-liquid volume" intersects either side-planes or solid saturation surfaces. Figs. 20 and 21 show modifications of Figs. 18 and 19, which agree more closely with the facts as mentioned. Only a portion of binodal surface 1 is shown, this corresponding with the surface $XNRSK_1TUMYI'K_2Q$ of Figs. 11 and 14. The critical curve of this surface, lettered K_1, terminates at the points K_1 and K_2 of Fig. 11. One of the other surfaces

Fig. 22.
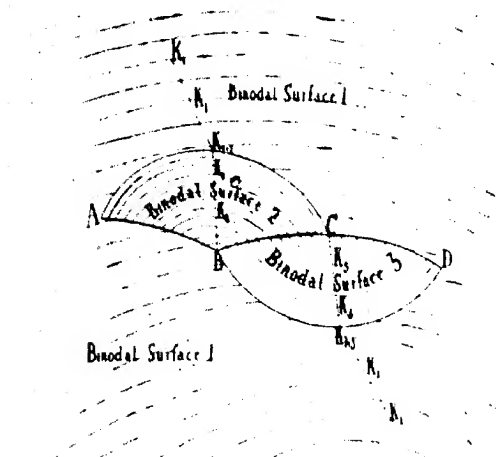
gives rise to the curves cpd and fng of Fig. 11, which show that the surface is not intersected across its critical curve. These intersections are not shown in Figs. 20 and 21, the significance of which is readily understood by reference to Figs. 18 and 19, to which they bear a close resemblance.

Fig. 22 shows the three binodal surfaces in positions which give rise to curves of intersection having the same relative positions as those of Fig. 17, and since it represents the actual equilibrium so nearly it will be well to consider it in some detail. The letters correspond with those of the preceding figures, AB, BC, and CD again representing the three curves of conjugate liquids. Surface 1, of which part only is shown, corresponds with

$$XNRSK_1TUMYI'K_2Q$$
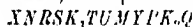
of Figs. 11 and 14, and can be considered as lying in the plane of the paper. The stable portions of the two binodal surfaces intersecting it are shown by $AK_{1+2}CB$ (No. 2) and $BCDK_{1+3}$ (No. 1). AB is the curve of intersection of surfaces 1 and 2, BC that of surfaces 2 and 3, CD that of surfaces 3 and 1. AB and CD therefore lie on surface 1, that is, in the plane of the paper, which only touches it at its end-points, B and C. $AK_{1+2}C$ is the curve along which only surfaces 1 and 2 intersect, $BK_{1+3}D$ that along which only surfaces 1 and 3 intersect. They therefore lie on surface 1, and are both critical curves.

The parts into which the space enclosed by the binodal surface is divided are four in number, as follows:

(1) The two-liquid space representing mixtures of two conjugate liquids lying on surface 1. This is bounded by the binodal surface itself, and the surface $ABCD$, formed by joining all pairs of conjugate points on AB and DC. It has already been defined as the space formed by joining all pairs of conjugate points on the binodal surface.

(2) The two-liquid space representing mixtures of two conjugate liquids lying on surface 2. This is bounded by the binodal surface itself, $ABCK_{1+2}$, the surface $AK_{1+2}C$ formed by joining all pairs of conjugate points on AK_{1+2} and CK_{1+2}, and the surface AB formed by joining all pairs of conjugate points on AB and C. The space is thus formed by joining all pairs of conjugate points on the binodal surface.

(3) The two-liquid space representing mixtures of two conjugate liquids lying on surface 3. This again is formed by joining pairs of conjugate points on the binodal surface. It is bounded by the binodal surface itself, together with the surface BK formed by joining all pairs of conjugate points on BK_{1+3}, DK_{1+3}, and the surface BCD formed by joining all pairs of conjugate points on BC and DC.

(4) The three-liquid space, representing mixtures of three conjugate liquids lying on AB, BC, and CD respectively. It is bounded by the surface $ABCD$, formed by joining all pairs of conjugate points on AB and DC; the surface BCD formed by joining all pairs of conjugate points on BC and DC; and the surface ABC, formed by joining all pairs of conjugate points on AB and CB. The three-liquid space thus lies inside the surfaces formed by joining all sets of conjugate points on AB, BC, and CD.

A consideration of Fig. 22 shows that the triangular planes formed by joining three conjugate points on AB, BC, and CD respectively are not parallel to one another. If a plane is drawn

as to intersect the three-liquid space, it may cut the three conjugate curves in points which are either conjugate or not conjugate with one another. The intersecting planes to be considered are those representing mixtures in which ether and water bear a constant ratio to one another, such as ADL in Fig. 11, and those parallel to one side of the tetrahedron, representing mixtures of a constant percentage of one particular component.

Fig. 23 is a section formed by a plane such as ADL in Fig. 11, passing through the three-liquid space and across the three conju-

FIG. 23.
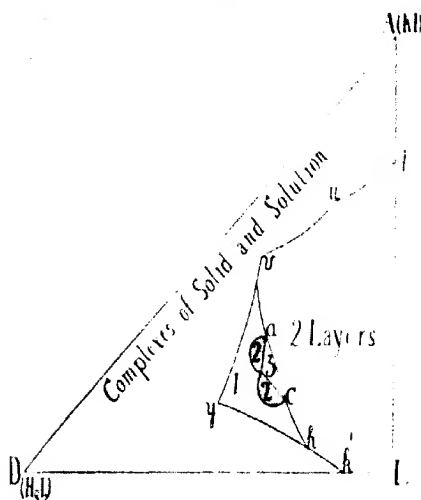
to curves at a, b, and c respectively. The section of the three-liquid space is shown on a larger scale in Fig. 24.

We will first consider the case in which a, b, and c are conjugate to one another. The significance of the areas into which EBK_2G is divided will be clear from what has already been said with regard to the sections in Figs. 19 and 21. When a definite mixture of the two solid components is added little by little to the liquid mixture I_0, the mixture so formed follows a straight line continuing ADL, such as $rxyw$ in Fig. 24. As it moves along r the two layers into which it separates follow Ra and Gc respectively, so that when the mixture is represented by r the layers are represented by a and c. When the mixture moves from r along

vs it enters the three-liquid area, and a third liquid, *c* separate, *a* and *c* remaining unchanged in composition. As *b* approached *b* increases in amount, whilst *c* decreases, layer *c* entirely disappears, leaving *a* and *b*. As the mixture follows *sy*, the two layers follow aK_2 and bK_2 respectively, only solution *y* is left, the other quite disappearing. The homogeneous liquid then follows *yw*, eventually, of course, saturated. It is obvious that either the layer on aK_2 or that on bK_2 can disappear, or they can become identical, according to the position of the point *y*, at which *rrsyw* cuts the curve aK_2. When the mixture follows the line *efghk* the phenomena occurring is

Fig. 24.

similar. Of the three-liquid layers, *a*, *b*, and *c*, however, a disappears, leaving only *b* and *c* when the mixture reaches ...

When the mixture follows a line such as *pmbq*, passing ... *b*, a slightly different behaviour occurs. At *m*, *a* and *c* separates the two layers, and as the mixture follows *mb*, the third layer separates, and increases in amount whilst *a* and *c* decrease ... *b*, *a* and *c* disappear simultaneously, leaving only *b*, which traverses the homogeneous area along the line *bq*.

When the plane intersects the three-liquid space in ... that *a*, *b*, and *c* are not conjugate points, the section ... similar in form to that shown in Fig. 24, is no longer of ... quantitative interpretation. Thus, a point inside the ... *abc* represents a mixture of three layers, but these are not ...

... by the **points** *a*, *b*, and *c*. The plane cuts across a number
... triangles, so that as the mixture follows the line *es*
... the three **layers** change, not only in amount, but in composi-
... Similarly, **the** compositions of the layers composing mixtures
... two-liquid **areas** are not given by points on the bounding
...

... plane can **intersect** the three-liquid space in a variety of ways,
... rise to **various** special forms of sectional curves, such as those
... when **the** plane intersects the three-liquid space without
... all **three** conjugate curves (*AB*, *BC*, and *CD*). The forms
... various **sections** can be readily determined, and will not
... considered **here**.

MMII.—*Resolution of* trans-cyclo*Pentane* 1 : 2-*di-
carboxylic Acid.*

By LEONARD JAMES GOLDSWORTHY and WILLIAM HENRY
PERKIN, jun.

... accordance with **the** theory of Le Bel and van't Hoff, many
... dicarboxylic **acids** of the cyclic hydrocarbons should be
... of resolution **into** optically active modifications. Hitherto,
... two acids **of** this type have been investigated in this respect,
... the first to be resolved was *trans*-hexahydrophthalic acid:

$$CO_2H \quad H$$

$$CH_2 \cdot CH_2 \cdot C$$
$$CH_2 \cdot CH_2 \cdot C$$

$$H \quad CO_2H$$
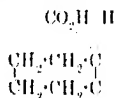
In 1899, Werner and Conrad (*Ber.*, **32**, 3046) showed that this
... compensated acid may be resolved into its active
... by the fractional crystallisation of the quinine salts.
... the active acids were found to have α_D, +18·2° and −18·5°
respectively. These investigators also showed that, whilst the ex-
... compensated acid is almost insoluble in water and melts

at 215°, the d- and l-modifications melt at 179--183
much more soluble; again, the anhydrides of the active
at 164°, or considerably higher than that of the dl-acid
melts at 140°. Furthermore, the conversion of the acids
their anhydrides is attended by a reversal and at the same
considerable increase of the rotation, since the d-acid
yields an anhydride with a_D $-76.7°$; the dimethyl esters
same sign as their acids and the rotations a_D $+28.6°$
respectively. At a later date (*Ber.*, 1905, **38**, 311),
and von der Heide investigated *trans-cyclopropane*
oxylic acid,

$$CH_2 \diagdown \begin{matrix} CH \cdot CO_2H \\ CH \cdot CO_2H \end{matrix}$$
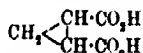
and showed that this acid can be resolved into its active
ponents by the fractional crystallisation of the salts with
quinine, or cinchonidine. The active acids melt at
at the same temperature as the dl-acid, and have a_D
attempts to prepare the anhydrides of these acids have
successful, since they distil unchanged and are not
acetyl chloride.

Some years ago, a series of experiments was
the Laboratories of Manchester University by one
junction with Mr. H. D. Gardner with the object of
the resolution of *trans-cyclo*pentane-1:2-dicarboxylic acid,

$$CH_2 \diagdown \begin{matrix} CH_2 \cdot CH \cdot CO_2H \\ CH_2 \cdot CH \cdot CO_2H \end{matrix}$$
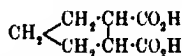
(*Perkin*, T., 1887, **51**, 244), but the investigation
completed.

We have now taken up the subject again and find that
may be readily and completely brought about with the
brucine.

When the dl-acid is combined with brucine and the
are recrystallised from water, the salt of the d-acid
and is readily obtained pure by repeated recrystallisation
l-acid may then be recovered from the mother liquors
manner described on p. 2643. The observed rotations of the
l-modifications were a_D $+87.6$ and -85.9 respectively, and
of the corresponding ethyl esters, a_D $+70.31°$ and $-69.7°$
d- and l-modifications of *cyclo*pentane-1:2-dicarboxylic
at 181° or 21° higher than the melting point of the
tion (m. p. 160°). For the sake of ready comparison, the
and melting points of the *trans-cyclo*propane-, pentane-
-hexane-1:2-dicarboxylic acids are appended in tabular for

	a_D d acid.	a_D l acid.	M. p. of d- and l- acids.	M. p. of inactive acid.
cycloPropane-1:2-dicarboxylic acid	+ 84·9°	84·5	175	175°
cycloPentane-1:2-dicarboxylic acid	+ 87·6	85·9	181	160°
cycloHexane-1:2-dicarboxylic acid	+ 18·2°	18·5	178—183°	215°

would be interesting to fill up the gap between *trans-cyclo-pane* 1:2 dicarboxylic acid and the corresponding *cyclopentane-carboxylic* acid by the resolution of *trans-cyclobutane* 1:2 dicarboxylic acid,

$$CH_2 \cdot CH \cdot CO_2H$$
$$CH_2 \cdot CH \cdot CO_2H$$
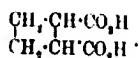
unfortunately, the preparation of this acid (T., 1894, **65**, 585) quantity sufficient for resolution is most troublesome and, though experiments with this object have been commenced, we have not yet been able to separate the active modifications in a pure state

EXPERIMENTAL.

d-trans-cyclo*Pentane*-1:2-*dicarboxylic* Acid.

The *dl trans-cyclo*pentane-1:2-dicarboxylic acid employed in my experiments was prepared by the method described by Perkin (T., **51**, 240; compare T., 1894, **75**, 586). The pure acid, quantities of 15 grams, dissolved in hot water, was mechanically stirred and brucine (90 grams) gradually added, when the alkaloid may dissolved. The excess of brucine was filtered off, well washed with hot water, and the filtrate and washings were concentrated on the water-bath until crystals just commenced to form the surface. When the liquid was cooled and vigorously stirred, copious crystallisation took place, and the whole became semi-solid; the crystals were then collected and repeatedly recrystallised from hot water. During this operation, the progress of the separation of the brucine salt of the *d*-acid from that of the *l* modification was followed with the polarimeter, and the table given below shows that the separation is nearly complete after six crystallisations, since the difference between the rotation of this crop and of that obtained as the result of the twelfth crystallisation very small.

No. of crystallisation.	Weight of substance. Gram.	Observed rotation.	Specific rotation.
1st crop	0·5250	−1·68°	−32·1°
3rd ,,	0·4566	−1·14°	−25·0°
4th ,,	0·5050	−1·15°	−22·8°
5th ,,	0·2612	−0·51°	−19·9°

A specimen of the pure brucine salt was subsequently prepared by adding excess of brucine to the hot dilute aqueous solution of the pure *d*-acid (see below), and, after filtering, the solution was allowed to crystallise slowly over sulphuric acid, when large, brilliant, tabular crystals separated. As these crystals effloresce in a vacuum desiccator, they were dried by exposure to air and then analysed:

0·1314 gave 0·2782 CO₂ and 0·0859 H₂O. C=57·7; H = ;
0·5079   ..   22·6 c.c. N₂ at 19·8° and 753 mm. N = ;
2C₂₃H₂₆O₄N₂,C₅H₁₀O₄,9H₂O requires C = 57·4; H = ; N

per cent.

That the salt has this composition was confirmed by the fact that 0·2316 gram, heated for one hour at 125°, lost 0·032 g., whereas the calculated loss for 9H₂O is 0·0339 gram.

In order to obtain the pure *d*-acid, the brucine salt from the twelfth crystallisation was dissolved in hot water, the base precipitated by ammonia and, after filtering and washing, the solution of the ammonium salt was concentrated and acidified with hydrochloric acid when, on cooling, the *d*-acid separated in plates, and melted at 178—180°. After completely purified with the aid of animal charcoal, and twice crystallised from water, the acid melted at 181°, and 0·1752 dissolved in water (20 c.c.) gave, in a 2-dcm. tube, a rotation of 1·53°, whence a₀ +87·6°. On titration, 0·1778 required 0·0898 N. NaOH neutralisation, whereas this amount of an acid, C₅H₁₀O₄, should neutralise 0·0900 NaOH.

The d-*ethyl ester*, C₅H₈(CO₂Et)₂, was prepared by the *d*-acid with five times its weight of 10 per cent. alcoholic acid for six hours; water was then added, the ester extracted with ether, and, after washing with water and dilute sodium carbonate, the ethereal solution was dried, evaporated, and the ester distilled under diminished pressure.

It boiled constantly at 170°/100 mm., and 0·2596 dissolved in acetone (20 c.c.), gave, in a 2-dcm. tube, a rotation of 1·8° whence a₀ = 70·31°.

The d-*Anilide*, C₅H₈(CO·NH·C₆H₅)₂. In order to prepare this derivative, the *d*-acid was heated with thionyl chloride in a sealed tube in boiling water for an hour, the clear liquid evaporated on the water-bath, and the residual acid chloride dissolved in benzene and mixed with excess of aniline. The benzene was removed by evaporation, the residue stirred with dilute hydrochloric acid, and the crystalline precipitate collected and recrystallised from

methyl alcohol, in which it is sparingly soluble, separating as a luminous mass of needles melting at 245—247° (uncorr.):

0.2756 gave 21·7 c.c. N_2 at 18·4° and 762 mm.   N   9·1.

$C_{19}H_{26}O_3N_2$ requires N   9·1 per cent.

This, dissolved in acetone (20 c.c.), gave, in a 2-dcm. tube, a rotation +1·880°, whence α_D = 110·1°.

Attempts which were made with the object of preparing the anhydride of the *d-trans* acid were not successful and the results obtained seem to throw some doubt on the existence of this anhydride. Since, however, *trans*-cyclohexane-1 : 2-dicarboxylic acid (*cis*-hexahydrophthalic acid) yields an anhydride without difficulty (Baeyer, *Annalen*, 1890, **258**, 179), there is every reason to suppose that the anhydride of *trans*-cyclopentane-1 : 2-dicarboxylic acid should also be capable of existence, but it is doubtful whether the substance described by Haworth and Perkin (T., 1894, § 986) can be accepted as this anhydride.

l-trans-cycloPentane-1 : 2-dicarboxylic Acid, l.

In order to obtain this acid, the mother liquors from the first crystallisations of the brucine salt of the *dl* acid (p. 2641) were concentrated until crystals began to appear on the surface of the warm liquid. The salt, which separated in quantity on cooling, is dissolved in hot water, the solution decolorised with animal charcoal, and the crude *l* acid isolated in the manner described in the case of the *d*-acid.

The acid is readily obtained pure simply by recrystallising four times from water, it then melted sharply at 180—181°, and 0·2363, dissolved in water (20 c.c.), gave, in a 2-dcm. tube, a rotation of −2·3°, whence α_D −85·9°. On titration, 0·3110 required 0·1568 NaOH for neutralisation, whereas this amount of an acid, $C_7H_{10}O_4$, should neutralise 0·1575 NaOH.

The *ethyl ester*, $C_5H_8(CO_2Et)_2$, obtained in the manner described in detail in the case of the ester of the *d*-acid, distilled at ° but mm., and 0·3326, dissolved in acetone (20 c.c.), gave, in a 2-dcm. tube, a rotation of −2·32°, whence α_D −69·76°.

THE UNIVERSITY MUSEUM,
    OXFORD.

CCXLVIII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part IX. The Rotatory Powers of 1-Naphthyl-phenyl-carbinol and its Esters.*

By Joseph Kenyon and Robert Howson Pickard.

THIRTY EIGHT optically active carbinols of the formula

$$R_1 \cdot CH(OH) \cdot R_2$$
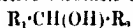
have been described so far in this series of investigations, and with one exception have been shown to possess certain characteristics as regards dispersive power. Thus their rotatory powers for light of wave-length ranging from that of sodium yellow to that of mercury violet not only increase continuously with decreasing wave-length (that is, the compounds exhibit what is commonly spoken of as *normal* dispersive power), but also conform to the law of simple dispersion expressed by Drude's equation with one term, $a = k/\lambda^2 - \lambda_0^2$ (compare Lowry, Pickard, and Kenyon, this vol., p. 94). Further, a dispersion ratio, such as, for example Hg_{green}^{violet} is in the cases of many of the carbinols approximately constant over a range of temperature extending up to their boiling-points, and even in the others varies only to a very slight extent, whilst the dispersion ratio is only affected to a very slight extent by solvents. It is probable, however, that this is a special property of this class of compounds, the rotatory powers of which are not affected to any large extent by increase of temperature or solvent. Indeed, on reference to the "characteristic diagrams" (for example see Part V., this vol., p. 847) for a homologous series of these carbinols these properties appear as an obvious arithmetical fact, since the violet and green lines of the diagrams intersect so near to the zero. It should, however, be borne in mind that the method of plotting rotation data known as "characteristic diagrams" developed by the present authors for the correlation of the rotation data of many compounds of allied structure—whilst proving extremely useful in several directions—is, however, largely empirical, having been devised originally on theoretical grounds by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [A], **88**, 388) to aid in the explanation of the *anomalous* dispersion of a compound by assuming the presence in it of two dynamic isomerides of different optical properties.

It also seems desirable to suggest that inferences drawn from

...ations in the magnitude of a dispersion ratio are likely to prove ...ading, whilst the use of negative and positive signs for such ...ios in the region of what is commonly known as anomalous ...persion has apparently no meaning whatever.

Among the carbinols referred to above the conspicuous excep... is l-naphthylmethylcarbinol (Part VI., this vol., p. 1116). ...e rotations of this compound appear to obey the law of simple ...persion only at temperatures above 160°, whilst in the super-...oled state the carbinol exhibits the phenomenon known as anoma-...us dispersion at and below a temperature of about 10°. So ...traordinary, then, are the optical properties of this carbinol that ...med desirable to investigate some of its homologues, but owing ... the many experimental difficulties only $d\,l$ naphthyl n hexyl-...binol has been prepared.

The properties of the new carbinol are quite analogous to those ...the corresponding methyl compound. Thus in the homogeneous ...te (see Fig. 1 and table I) the dispersion is "anomalous" (for ...low to violet light) at temperatures between about 22° and 38°, ...t the rotations conform to the law of simple dispersion at about ...d above a temperature of 180°. The regular character of the ...ation curves seems to negative any suggestion that the anoma-...us dispersion is due specially to polymerisation in the neighbour-...d of the melting point of the carbinol, although they show that ...e cause of the "anomaly" is gradually removed by increase of ...mperature

The majority of chemists appear to favour the explanation of ...malous dispersion in compounds of simple constitution by the ...mption of the presence in what is otherwise the homogeneous ...pound of two dynamic isomerides differing in optical sign and ...tatave power. It has been suggested already (Part VI., loc. cit.) ...t in the case of these naphthylcarbinols such isomerides are ...sed by a difference in the disposition of the valencies in the ...ethyl radicle. An alternative suggestion made by Patterson ...913, 103, 145) that this phenomenon is due to a succession ...maxima and minima on the rotation curves occurring at different ...peratures for light of various refrangibilities, whilst very diffi-...lt of direct experimental test, is nevertheless rendered very ...btful in the authors' opinion by the accumulation of data ...cited in these investigations.

...It has now been shown that the presence in an optically active ...pound of a naphthyl group attached at the "α"-position or ...an esterified carboxylic group is associated very frequently with ...phenomenon of anomalous dispersion. In each case tempera-

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ture has a great effect on the phenomenon, increase of temperature destroying it in the case of naphthyl compounds, but bringing it to view in the case of the esters. It is desirable, however, that the term "anomalous" dispersion should no longer be used. Portions

FIG. 1.

Temperature.
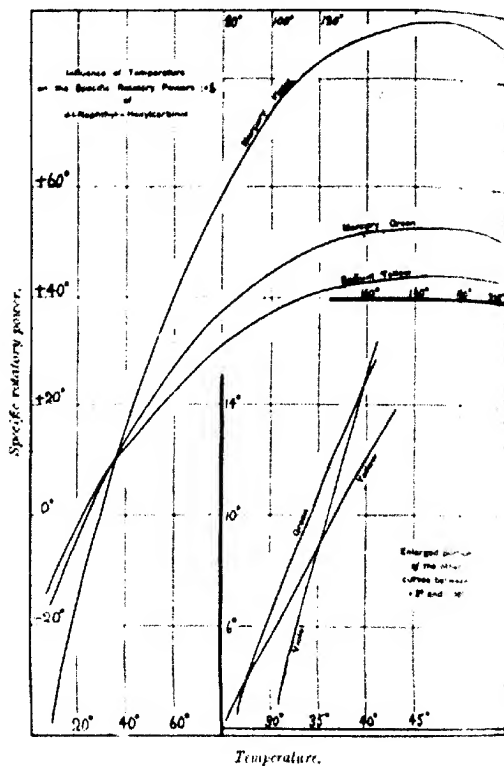
of the rotation curves on either side of the region of "anomalous" dispersion have dispersion ratios which rapidly increase or decrease. "Anomalous" dispersion as commonly understood refers as a rule merely to portions of the rotation curves artificially selected according to the wave-lengths of light under consideration. In view

Lowry's work (T., 1913, **103**, 1067 *et seq.*) it is much better to use only the terms *simple* and *complex* as applied to dispersive power according as the rotations conform to Drude's equation with one or more terms.

Among the large number of compounds studied in these investigations the 1-naphthylcarbinols at low temperatures and the esters described in the authors' previous communications at high temperatures tend, then, to exhibit *complex* dispersive power, the dispersive power becoming *simple* in each case if the conditions of temperature are reversed.

These generalisations * are confirmed by the optical properties of the esters of the two naphthyl carbinols with normal fatty acids, since it has been found that the acetate of *l*-1-naphthylmethyl-carbinol and a homologous series of esters (ranging from the acetate to the *n*-undecoate) of *d*-1-naphthyl-*n*-hexylcarbinol each exhibits complex dispersive power at all temperatures from 20° to 200°, the limits of the experimental conditions. The dispersion ratios for these esters are not affected much by temperature, and are nearly identical throughout the series. This is noteworthy, not only for the exceptions, but also as occurring in a series all members of which have complex dispersions. The dispersion ratios of each ester, however, are about 5 per cent. greater in carbon disulphide solutions than in the homogeneous state.

The configurations ascribed to *l*-1-naphthylmethylcarbinol and *l*-naphthyl-*n*-hexylcarbinol, although these compounds and some their derivatives are under certain conditions dextro- and lævo-rotatory respectively, are justified by drawing the characteristic gram for each carbinol, when it will be found that the two grams form exact mirror images of one another. As has been already mentioned, such diagrams are based on the assumption the presence in the carbinols of two dynamic isomerides differing optical sign and dispersive power, but in the case of the esters these carbinols there may be assumed to be present four dynamic isomerides in each ester. It is therefore not surprising that the rotation data for the esters recorded in the experimental part not be correlated on the characteristic diagrams of the carbinols, though these four dynamic isomerides would in pairs have the same optical sign.

* The authors are aware that many of the generalisations stated in this and in other papers of the series are open to the criticism that the same are based on rotatory readings of small magnitude. However, they feel that the concordant results which have now been obtained for a very large number of compounds justify these generalisations.

The trend of the values of the molecular rotatory powers of the members of this series of esters is dissimilar to those of the other

Number of carbon atoms in acyl group.
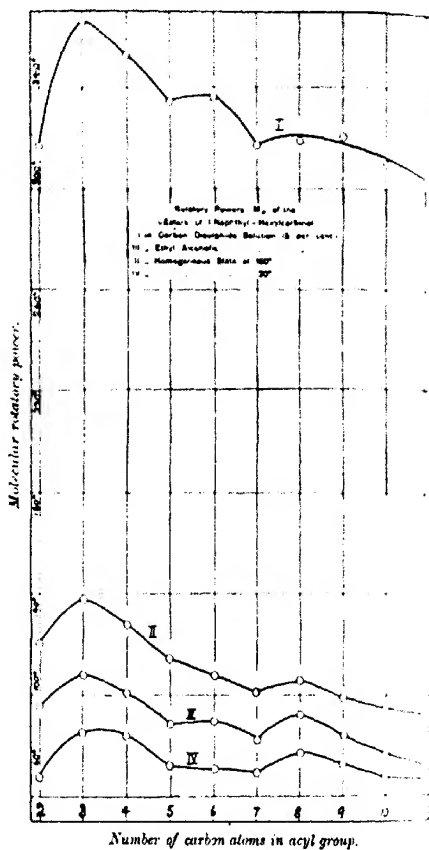
series of esters described in these investigations. Thus it will be seen from Fig. 2 that the curves connecting molecular weight and molecular rotatory power determined under several conditions (

temperature and solution show maxima at the propionate and valerate in addition to the maximum so commonly exhibited at the

Fig. 3.
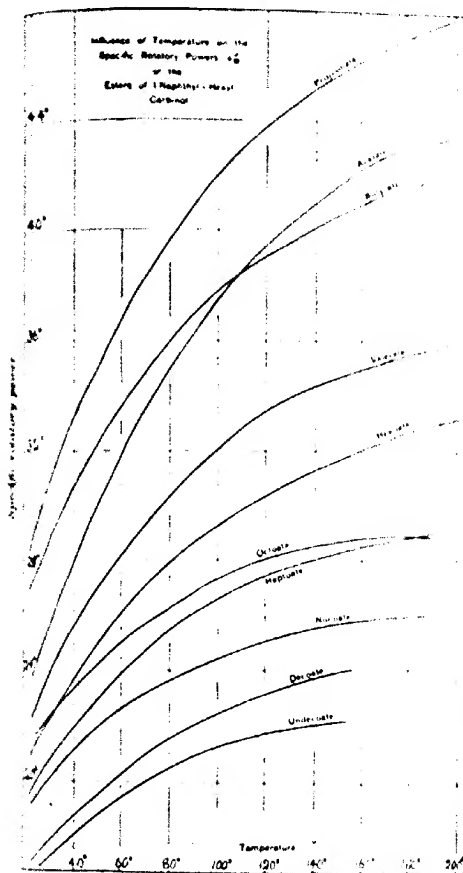
valerate (or valerate). This somewhat irregular result is perhaps less surprising in a series of esters of such complexity, that is, as compared to the esters previously described, which have been those

of carbinols of simple structure (compare, however, Part III. _
1912, **101**, 1430). To explain this is difficult, but it is significant
that the maxima at the propionate and octoate follow one another
at points in the series in the interval between which the chain is
grown by five carbon atoms, that is to say, at the octoate the
growing chain may be assumed to have all but returned to the
position occupied by it in the propionate. It is, however, possible
that the mass of the growing chain as it approaches (or just exceeds
that of one of the other groups (for example, the hexyl or naphthyl
group) may have an additional effect on the molecular rotatory
power and cause some special exaltation.

In Fig. 3 the effect of temperature on the rotatory powers of the
esters is illustrated. In general this effect (within the experimental
limits) is a common one on all the members of the series, although
there is a significant change of slope in the curve for the octoate

TABLE I.

d-1-Naphthyl-n-hexylcarbinol.

Temperature.	D_4^t	$[\alpha]_{5461}^t$	$[\alpha]_D^t$	$[\alpha]_{HI}^t$	$[M]_{5461}^t$	$[M]_D^t$	$[M]^t$. H_2
10°	1·0310	−11·26°	−14·89°	−40·25°	−27·24°	−36·03°	−97·40	· · ·
20	1·0232	−1·51	−2·05	−12·75	−3·66	−4·97	−30·85	5·11
40	1·0075	+12·46	+13·85	+16·92	+30·15	+33·52	+40·96	1·22
60	0·9911	23·29	26·89	40·41	56·35	65·07	97·79	1·42
80	0·9754	31·22	37·47	58·95	75·54	90·67	142·7	1·72
100	0·9600	37·50	44·37	72·95	90·74	107·4	176·5	1·84
120	0·9444	41·03	48·78	82·58	99·28	118·0	199·8	1·92
140	0·9285	42·71	51·34	87·26	103·4	124·3	211·2	1·78
160	0·9129	43·82	52·86	89·82	106·0	127·9	217·4	1·66
180	0·8970	44·13	53·67	90·86	106·8	129·9	219·9	1·70
200	0·8813	42·62	51·06	86·26	103·0	123·6	208·6	1·93

Table II.

Acetate of d-1-Naphthyl n hexylcarbinol.

Temperature	D_t^t	$[a]_{t}^{1}$	$[a]_{t}^{1}$	$[a]_{t}^{1}$	$[a]_{t}^{1}$	$[M]_{t}^{1}$	$[M]_{t}^{1}$	$[M]_{t}^{1}$	$[M]_{t}^{1}$	Dispersion ratios.	
										Hg_{green}	Hg_{violet}
20°	1·0262	+23·85°	+25·05°	+28·68°	+53·10°	+67·74°	+71·15°	+81·45°	+151·0°	1·148	1·854
40	1·0110	28·15	29·56	34·07	63·16	80·05	83·95	96·67	179·4	1·153	1·854
60	0·9947	32·12	33·50	38·73	71·58	91·22	95·13	110·0	203·2	1·154	1·848
80	0·9785	35·10	36·89	42·48	79·18	99·68	104·7	120·6	224·9	1·153	1·866
100	0·9624	37·75	39·51	45·50	84·78	107·2	112·2	128·2	240·7	1·154	1·863
120	0·9460	39·64	41·78	48·09	89·41	112·6	118·7	130·6	253·9	1·154	1·859
140	0·9300	41·20	43·44	50·03	93·07	117·0	123·4	142·1	264·3	1·158	1·860
160	0·9139	42·35	44·42	51·39	95·45	120·2	126·2	145·9	271·1	1·157	1·858
180	0·8979	43·10	44·82	51·84	97·12	122·4	127·3	147·2	275·2	1·155	1·866
200	0·8815	43·34	44·84	51·40	97·90	123·1	127·4	145·6	278·1	1·153	1·903

Propionate.

20°	1·0147	+28·50°	+30·18°	+34·69°	+64·36°	+85·17°	+89·93°	103·4?	191·6°	1·149	1·856
40	1·0002	33·93	34·43	39·94	74·03	95·11	102·6	119·1	220·6	1·160	1·854
60	0·9850	36·65	38·13	44·39	83·91	109·2	113·8	132·3	247·4	1·162	1·869
80	0·9692	39·62	41·28	47·92	89·76	113·9	123·0	142·8	267·5	1·161	1·874
100	0·9521	42·07	43·96	50·76	95·54	125·4	131·0	151·2	284·7	1·154	1·882
120	0·9339	43·82	45·73	52·91	99·49	130·4	136·2	157·7	296·2	1·157	1·878
140	0·9150	45·17	47·20	54·70	102·7	134·6	140·6	163·0	305·9	1·159	1·876
160	0·8961	46·24	48·35	56·19	105·1	137·8	144·1	167·4	313·1	1·162	1·889
180	0·8778	47·08	49·12	57·03	107·9	140·3	146·4	169·9	318·8	1·161	1·876
200	0·8595	47·73	49·71	57·51	109·1	142·3	149·1	171·4	322·2	1·157	1·876

TABLE II (continued).

n-Butyrate.

Temperature	D.	[α]ᵢ	[α]ⱼ	[α]ₖ	[α]ₗ	[M]ᵢ	[M]ⱼ	[M]ₖ	[M]ₗ	Hg green	Hg violet
										Hg yellow	Hg green
20°	1·0050	+27·02°	+28·16°	+32·54°	+60·22°	+84·29°	+87·88°	+101·5°	+187·9°	1·155	1·850
40	0·9899	30·71	32·15	37·16	69·34	95·83	100·3	116·0	216·4	1·156	1·866
60	0·9744	33·71	35·44	41·00	76·08	105·2	110·6	127·9	238·2	1·157	1·871
80	0·9587	36·02	37·86	44·11	81·93	112·4	118·1	137·0	255·7	1·165	1·858
00	0·9431	37·87	39·77	46·15	86·24	118·1	124·1	144·0	269·1	1·161	1·868
20	0·9273	39·13	41·22	47·69	89·02	122·1	128·6	148·8	277·7	1·157	1·871
40	0·9116	40·17	42·27	48·84	91·49	125·3	131·9	152·7	285·5	1·158	1·869
60	0·8957	41·04	43·11	49·82	93·42	128·0	134·5	155·4	291·5	1·155	1·873
180	0·8800	41·66	43·75	50·46	94·58	130·0	136·6	157·4	295·1	1·153	1·876
200	0·8643	42·01·	44·10	50·71	94·99	131·6	137·6	158·2	296·4	1·150	1·874

n-Valerate.

Temperature	D.	[α]ᵢ	[α]ⱼ	[α]ₖ	[α]ₗ	[M]ᵢ	[M]ⱼ	[M]ₖ	[M]ₗ	Hg green	Hg violet
										Hg yellow	Hg green
20°	0·9974	+22·23°	+23·30°	+26·73°	+49·45°	+72·47°	+75·96°	+87·14°	+161·2°	1·148	1·850
40	0·9816	25·42	26·65	30·71	57·68	83·85	86·86	100·1	188·0	1·153	1·878
60	0·9660	28·19	29·53	34·09	64·30	91·89	96·27	111·1	209·6	1·154	1·887
80	0·9500	30·47	31·84	36·74	69·00	99·31	103·8	119·8	224·9	1·153	1·878
100	0·9348	32·18	33·67	38·89	72·40	104·9	109·7	126·8	237·0	1·154	1·869
120	0·9191	33·47	35·10	40·52	75·88	109·1	114·4	132·1	247·4	1·154	1·873
140	0·9035	33·45	36·08	41·73	78·11	112·3	117·6	135·6	254·6	1·150	1·872
160	0·8871	35·11	36·73	42·48	79·50	114·5	119·8	138·6	259·2	1·162	1·872
180	0·8717	35·51	37·43	43·04	71·00	115·0	121·0	140·0	262·2	1·162	1·875
200	0·8550	36·00	37·94	43·94	77·00	116·0	121·5	140·9	264·2	1·163	1·884

TABLE II (continued).

n-Hexoate.

Temperature	D'_4	$[\alpha]_r$	$[\alpha]_r$	$[\alpha]_r$	$[M]_r$	$[M]_r$	$[M]_r$	Dispersion Hg/Li
20°	0·9994	+21·12°	+22·36°	—	+71·81°	+76·02°	—	—
40	0·9853	23·70	25·10	—	80·87	85·35	—	—
60	0·9595	26·35	27·76	—	89·60	94·39	—	—
80	0·9433	27·94	29·53	—	94·99	100·4	—	—
100	0·9272	29·34	31·06	—	99·74	105·6	—	—
120	0·9112	30·37	32·16	+37·74°	103·2	109·3	+128·3°	1·142
140	0·8955	31·27	33·05	38·59	106·4	112·4	131·2	1·143
160	0·8800	32·02	33·78	39·39	108·8	114·8	133·9	1·144
180	0·8643	32·62	34·46		110·9	117·1		

n-Heptoate.

Temperature	D'_4	$[\alpha]_r$	$[\alpha]_r$	$[\alpha]_r$	$[M]_r$	$[M]_r$	$[M]_r$	Dispersion Hg/Li
20°	0·9830	+19·63°	+20·59°	+23·68°	+69·50°	+72·88°	+83·83°	1·130
40	0·9074	21·97	23·31	26·46	77·75	82·52	93·07	1·135
60	0·9518	24·11	25·31	28·77	83·35	89·62	101·9	1·137
80	0·9360	25·74	26·85	30·56	91·14	95·04	108·1	1·139
100	0·9200	26·83	28·03	31·96	94·99	99·22	113·1	1·140
120	0·9042	27·50	28·82	33·93	97·34	102·1	116·0	1·146
140	0·8886	28·02	29·39	33·76	99·19	104·0	119·5	1·149
160	0·8725	28·54	29·96	34·39	101·0	106·0	121·7	1·148
180	0·8570	29·05	30·51	35·50	102·8	107·0	123·9	1·148

TABLE II (continued).

n-Octoate.

Tempera-ture.	L.	$[\alpha]_{?}$	$[\alpha]_{?}$	$[\alpha]_{?}$	$[\alpha]_{?}$	$[M]_{?}$	$[M]_{?}$	$[M]_{+93\cdot67^{\circ}}$	$[M]_{+175\cdot0^{\circ}}$	Hg.	Hg green.
20°	0·9797	+21·13°	+22·11°	+25·46°	+47·50°	+77·75°	+81·36°	+93·67°	+175·0°	1·152	1·858
40	0·9650	23·44	24·67	28·39	53·27	86·28	90·78	104·4	196·0	1·151	1·877
60	0·9505	25·23	26·57	30·61	57·44	92·85	97·77	112·7	211·3	1·152	1·877
80	0·9357	26·44	27·93	32·15	60·49	97·29	102·8	118·2	222·6	1·151	1·882
100	0·9210	27·36	28·85	33·19	62·38	100·7	106·2	122·1	229·6	1·150	1·879
120	0·9060	29·05	29·47	33·91	63·57	103·2	108·4	124·8	234·0	1·151	1·875
140	0·8913	26·49	29·88	34·44	64·63	104·8	110·0	126·8	237·8	1·153	1·876
160	0·8766	28·75	30·14	34·81	65·69	105·8	110·9	128·1	241·7	1·155	1·847
180	0·8617	28·89	30·34	35·03	66·70	106·3	111·6	128·9	245·4	1·154	1·904

n-Nonoate.

Tempera-ture.	L.	$[\alpha]_{?}$	$[\alpha]_{?}$	$[\alpha]_{?}$	$[\alpha]_{?}$	$[M]_{?}$	$[M]_{?}$	$[M]_{+87\cdot40^{\circ}}$	$[M]$	Hg.	Hg green.
20°	0·9726	+19·06°	+19·68°	+22·88°	+72·85°	+75·19°	+87·40°			1·162	
40	0·9576	21·25	21·82	25·22	81·19	81·10	83·37	96·34		1·155	
60	0·9425	22·80	23·45	27·16	87·10	80·58	103·8			1·158	
80	0·9276	23·82	24·61	28·52	91·01	94·01	109·0			1·159	
100	0·9126	24·57	25·46	29·58	93·85	97·27	113·0			1·161	
120	0·8977	25·15	26·22	30·42	96·07	100·2	114·2			1·160	
140	0·8830	25·88	26·75	30·99	95·77	102·3	116·5			1·158	
160	0·8629	26·03	26·14	31·14	90·45	103·2	126·2			1·108	

TABLE II (continued).

n-Decoate.

Temperature.	D'.	[α]_f.	[α]_c.	[α]_r.	[M]_f.	[M]_c.	[M]_r.	Dispersion. Hg-ratio.
20°	0·9603	+17·13°	+18·09°	+20·90°	+67·82°	+71·66°	+83·37°	1·149
40	0·9540	18·89	19·82	22·88	74·81	78·47	90·59	1·153
60	0·9389	20·45	21·25	24·55	80·98	84·16	97·31	1·155
80	0·9237	21·65	22·45	25·92	85·74	88·88	102·7	1·154
100	0·9086	22·56	23·42	27·02	89·35	92·72	107·0	1·154
120	0·8937	23·18	24·08	27·86	91·81	95·39	110·4	1·157
140	0·8788	23·69	24·58	28·44	93·82	97·34	112·7	1·157
160	0·8635	24·08	25·04	28·95	95·39	99·18	114·7	1·157

n-Undecoate.

Temperature.	D'.	[α]_f.	[α]_c.	[α]_r.	[M]_f.	[M]_c.	[M]_r.	Dispersion. Hg-ratio.
20°	0·9014	+16·44°	+17·08°	+19·76°	+67·39°	+70·01°	+81·04°	1·157
40	0·9468	18·17	18·79	21·97	74·47	77·07	90·07	1·160
60	0·9325	19·63	20·24	23·28	80·48	82·99	95·43	1·164
80	0·9179	20·65	21·29	24·22	84·65	87·32	99·31	1·137
100	0·9031	21·35	22·04	25·02	87·54	90·36	102·6	1·136
120	0·8885	21·78	22·48	25·55	89·32	92·17	104·7	1·137

TABLE III.

Acetate of 1:1-Naphthylmethylcarbinol.

Temperature	D_4^t	$[\alpha]_{5461}^t$	$[\alpha]_{5893}^t$	$[\alpha]_{4358}^t$	$[M]_{5893}^t$	$[M]_{5461}^t$	$[M]_{4358}^t$	Dispersion $\frac{\text{Violet}}{\text{Green}}$
20°	1·1044	−32·28°	−38·90°	−73·79°	−69·07°	−83·24°	−157·9°	1·898
40	1·0898	39·51	47·47	88·04	84·55	101·6	188·4	1·858
60	1·0733	44·58	54·04	101·51	95·43	105·6	217·2	1·878
80	1·0552	49·18	59·39	113·02	105·2	127·1	241·9	1·903
100	1·0368	52·85	64·21	121·57	113·1	137·4	260·1	1·892
120	1·0185	55·22	67·07	126·02	118·1	143·5	269·7	1·879
140	1·0002	56·78	68·68	129·82	121·5	147·0	277·8	1·891
160	0·9820	58·11	70·33	132·02	124·4	150·5	283·8	1·886
180	0·9635	59·29	71·83	135·39	126·9	153·7	289·7	1·865

EXPERIMENTAL.

dl-1-*Naphthyl-n-hexylcarbinol*,
$C_{10}H_7 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$.

The reaction between magnesium 1-naphthyl bromide and α-hept-aldehyde proceeds smoothly only under certain conditions. The ethyl bromide should be free from the dibromide commonly present in the commercial product, and the aldehyde should be freshly distilled. The aldehyde, dissolved in ten times its volume of ether, should be added very slowly to an excess of a dilute ethereal solution of the bromide, which is at the time reacting with slightly less than the calculated amount of magnesium, the temperature of the whole being kept at that of a mixture of ice and salt. The products of the reaction should be poured on to a mixture of ice and dilute sulphuric acid as soon as the addition of the aldehyde solution is complete, and then immediately extracted with ether. Much naphthalene being formed in the reaction it is desirable to remove it along with the ether and unchanged aldehyde by distillation in a current of steam. The residue is then dissolved in ether, carefully dried, and fractionally distilled under a pressure of 3 mm. All the carbinol is in the portion passing above 160°, whilst the lower fractions contain the corresponding unsaturated hydrocarbon and the unchanged naphthyl oxide. In one series of operations, working with 620 grams of bromide and 228 grams of *n*-heptaldehyde, the yield of carbinol was 370 grams.

dl-*Naphthyl-n-hexylcarbinol* boils at 184°/4 mm., and on keeping sets to a crystalline mass, which crystallises from light petroleum in feathery needles melting at 41--42°. When guarded from the accidental access of crystal nuclei, it will remain for some time in the supercooled condition, but solidifies rapidly when seeded.

The *hydrogen phthalate*, prepared by the method described in Part IV. (*loc. cit.*, p. 1126), is only sparingly soluble in light petroleum, and is best crystallised from a mixture of this and acetone, from which it separates in slender needles melting at 103--104°:

0.2245 neutralised 0·0226 NaOH. M.W. = 397. Calc. M.W. 390.

Resolution of Hydrogen Phthalate.

The fractional crystallisation from acetone of the brucine salts of the (d + l) phthalic ester yields readily the salt of the *d* ester, the process being carried out in the manner previously described in detail (see *inter alia*, T., 1912, **101**, 634). The ester (514 grams)

was dissolved in warm acetone (1½ litres), digested with bran (614 grams), and set aside to crystallise. The first crop weigh 300 grams, and was then recrystallised six times. The secon crop weighed 160 grams, and was the pure *l*B*d*A salt, whith me and decomposes at 124—125°. Two successive series of operation with the mother liquors comprising respectively eight and te crystallisations yielded further lots of the salt amounting to 14 a 15 grams respectively. Samples of the salt from the thin a seventh crops of the first series of crystallisations and from a final crops of the second and third series yielded hydrogen pital ates which had respectively [*a*]$_D$ −23·01°, −22·46°, −22·4°, a −22·62° respectively in (approximately) 5 per cent. ethyl alcohol solution.

d-1-*Naphthyl*-n-*hexylcarbinol* boils at 178°/3 mm., solidifies i stellate nodules, and melts at 41·5°.

The corresponding d-*hydrogen phthalate* solidifies in crystall nodules, melts at 91°, and is soluble in all the common orga media. The crystalline *sodium* salt, which was obtained by g neutralisation of a solution of the ester in methyl alcohol wi sodium methoxide and subsequent removal of the solvent in a des cator, is decomposed by water.

Normal Esters of the Carbinol.—Of the esters prepared table IV) the acetate, propionate, and n-butyrate were obtained the interaction of the carbinol and the respective anhydrides, and the others were prepared by the action of the respective ac chlorides on solutions of the carbinol in pyridine. They are viscous liquids at the ordinary temperature, and have no odour, w the higher members of the series often develop a faint viol bloom, which is difficult to remove by redistillation, thus rende ing uncertain any polarimetric readings in the green, and par ticularly in the violet portions of the spectrum.

TABLE IV.

Esters of d-1-*Naphthyl*-n-*hexylcarbinol.*

	B. p.		D$_4^{20}$.	n$_D^{20}$.	(n−1)/d.M.	[α].	M
Acetate	167°/2·5 mm.		1·0262	1·5471	151·3	+23·85	·67
Propionate ...	169°/2	,,	1·0147	1·5403	158·7	26·59	43
n-Butyrate ...	184°/3	,,	1·0050	1·5365	166·6	27·02	45
n-Valerate ...	187°/2·5	,,	0·9974	1·5332	174·3	22·23	36
n-Hexoate ...	198°/2·5	,,	0·9894	1·5289	181·8	21·12	38
n-Heptoate ...	207°/3	,,	0·9830	1·5271	189·8	19·63	44
n-Octoate	214°/3	,,	0·9797	1·5249	197·1	21·13	33
n-Nonoate......	222°/4	,,	0·9726	1·5225	205·2	19·06	36
n-Decoate ...	224°/2·5	,,	0·9693	1·5208	213·0	17·13	36
n-Undecoate...	232°/2·5	,,	0·9614	1·5188	221·0	16·44	51

4:1 Naphthylen hexylcarbinol

Solvent	Length of tube, cm	Weight of solute in grams	α	α	α	$[\alpha]$	$[\alpha]$	$[\alpha]$	$[M]$	$[M]$	$[M]$	Dispersion
Benzene	22	1·0589	+8·70°	+10·48°	+18·25°	+74·67°	+89·97°	+156·7°	+190·7°	+217·7°	+279·1°	1·742
Acetone.............	10	0·6687	2·39	2·80	5·20	71·48	85·54	155·5	172·9	207·0	376·2	1·818
Ethyl alcohol	22	1·0666	7·69	9·39	16·52	85·37	80·02	140·8	158·2	192·6	340·6	1·818
Chloroform	22	1·0952	7·80	9·40	16·41	84·76	78·03	136·2	166·7	186·8	329·7	1·746
Carbon disulphide	22	0·9686	6·41	7·73	13·30	60·15	72·52	124·8	145·5	175·5	302·0	1·721
Ethylene dibromide	10	0·9219	2·51	2·95	5·30	54·46	64·00	115·0	131·8	154·9	278·2	1·797
Pyridine	20	1·0340	4·38	5·23	9·02	42·36	50·58	87·24	102·5	122·4	211·2	1·725

Hydrogen Phthalate.

Carbon disulphide	22	1·0106	8·37	10·09	18·90	75·26	90·72	170·0	293·6	353·6	603·0	1·874
Acetic acid	22	0·9900	2·75	3·23	5·22	25·25	29·66	47·94	98·49	115·7	186·9	1·016
Chloroform	22	1·1846	2·28	2·71	4·22	17·50	20·80	32·38	68·23	81·12	126·3	1·655
Benzene	22	1·0917	0·60	0·57	0·12	5·00	4·74	1·00	19·48	14·51	3·30	2·105
Pyridine	22	1·0454	−0·15	−0·36	−1·28	−1·30	−3·13	−11·14	−5·09	−12·22	−43·45	3·555
Ethyl alcohol ...	22	1·0326	−2·55	−3·25	−6·93	−22·46	−23·63	−61·02	−87·58	−111·6	−234·0	2·132

Sodium Salt of the Hydrogen Phthalate.

| Ethyl alcohol...... | 22 | 1·0595 | −3·50 | −4·14 | −7·37 | −29·35 | −35·52 | −63·24 | −129·0 | −146·3 | −280·5 | 1·780 |

Brucine Salt of the Hydrogen Phthalate.

| Ethyl alcohol .... | 22 | 1·0826 | −1·45 | 2·07 | −5·62 | −12·81 | −17·39 | −47·21 | −95·50 | −136·3 | −276·1 | 2·714 |

All solutions for the determinations of rotatory power recorded in this paper were prepared by making up about 1 gram of the substance to 20 c.c. with the solvent at the temperature of the laboratory, at which temperature all observations were made.

TABLE VI.

Determination of the Rotatory Powers of the Esters in (approx.) 5 per cent. Solution in Ethyl Alcohol.

Ester	Length of tube, cm.	Weight of solute in grams.	$a_{1\cdot}$ +	$a_{2\cdot}$ +	$a_{3\cdot}$ +	$a_{4\cdot}$ +	$a_{5\cdot}$ +	$[a]_{1\cdot}$	$[a]_{2\cdot}$ +	$[a]_{3\cdot}$	$[a]_{4\cdot}$ +	$[M]_{1\cdot}$ +	$[M]_{3\cdot}$ +	$[M]_{4\cdot}$ +	$[M]_{5\cdot}$ +	Dispersion Hg green
Acetate	20	1·1363	3·84°	4·02	4·64°	8·62°	33·80°	35·38°	40·84°	75·88°	95·98°	100·5°	116·0°	215·5°	1·858
Propionate	20	0·9503	3·45	3·60	4·17	7·65	36·31	37·88	43·88	80·52	108·1	112·9	130·8	240·0	1·835
Butyrate	22	1·1019	3·90	4·08	4·70	8·70	32·18	33·66	38·77	71·70	100·4	105·1	121·0	224·0	1·851
Valerate	20	1·1392	3·10	3·34	3·76	7·04	27·21	29·32	33·01	61·80	88·72	93·57	107·6	201·5	1·873
Hexoate	20	0·9768	2·50	2·67	3·05	5·85	26·52	27·33	31·23	59·89	90·16	92·04	106·2	203·6	1·918
Heptoate	20	0·9887	2·30	2·44	2·76	5·10	23·26	24·68	27·91	51·58	82·33	87·36	98·81	182·6	1·848
Octoate	20	0·9020	2·28	2·37	2·72	5·12	25·27	26·27	30·16	58·76	93·01	96·68	111·0	208·8	1·882
Nonoate	20	1·1589	2·55	2·65	3·05	5·74	22·01	22·87	26·32	49·63	84·07	87·36	100·6	189·2	1·842
Decoate	22	1·0001	2·15	2·27	2·53	—	19·54	20·64	23·00	—	77·39	81·72	91·07	—	—
Umberate	20	1·1230	2·02	2·12	2·41	4·80	17·90	18·88	21·60	42·74	73·76	77·39	87·08	175·2	1·902

TABLE VII.

Determination of the Rotatory Powers of the Esters in (approx.) 5 per cent. Solution in Carbon Disulphide.

Ester	Length of tube, cm.	Weight of solute in grams	α (4 lines)				[α] (4 lines)				[M] (4 lines)				Dispersion Hg...
Acetate	22	1.1251	13.80	14.51	16.95	33.10	111.5	117.3	137.0	208.2	316.7	333.1	380.0	761.7	1.014
Propionate	20	1.0157	12.48	13.12	15.31	24.83	122.8	124.1	130.7	293.6	306.0	384.9	449.0	874.8	1.048
Butyrate	20	1.0865	12.05	12.74	14.84	20.12	113.1	119.5	139.3	273.2	352.8	373.0	434.5	832.5	1.062
Valerate	20	0.9541	9.70	10.32	12.07	23.58	102.5	108.1	126.6	247.3	333.6	352.7	412.5	806.0	1.054
Hexoate	10	0.9485	4.70	4.87	5.68	11.40	99.10	102.7	119.8	240.4	327.0	349.1	467.1	817.4	2.005
Heptoate	10	1.2190	5.47	5.79	6.72	13.25	89.74	94.99	110.3	217.4	317.7	339.2	390.3	769.5	1.972
Octoate	10	1.0842	4.48	4.71	5.49	10.55	86.64	91.07	106.2	207.9	318.8	335.2	390.6	764.9	1.958
Nonoate	10	1.0209	4.29	4.52	5.34	10.40	84.06	88.54	104.6	203.8	321.0	348.2	399.6	775.2	1.947
Decoate	20	1.6773	5.43	5.77	6.77	21.50	7.36	82.35	96.20	189.6	310.3	326.1	781.0	790.5	2.025
Undecoate	22	1.0180	7.31	7.74	10.19	20.50	74.22	78.05	96.99	182.1	304.3	350.0	453.1	750.8	2.012

*Determinations of Density (D'₄) and Rotatory Power (α's ...
the Carbinol and Esters in the Homogeneous State.*

The procedure in the determinations of rotatory power and
density was the same as described in Part VIII. (this vol. ...

d-1-Naphthyl-n-hexylcarbinol.

Temp.	31˙	63°	91°	146°
D₄	1·0147	0·9890	0·9668	0·9234

Temp.	15˙	24˙	26·5˙	28˙	36°	38°	42·5°	44˙	49
aₙ ...	−6·04˙	−3·26	3·88˙	4·56	10·12°	11·40°	13·60°	14·94˙	17·5˙
	53˙	58˙	64°	76˙	98˙	104°	119°	145˙	169
	+20·00˙	22·00˙	25·14	29·10˙	35·72˙	36·52˙	38·80°	39·60˙	40·10˙

Temp.	15˙	24˙	25˙	26·5˙	28˙	32·5°	39°	43˙
aₘᵣ......	−8·12˙	−2·30°	2·48˙	3·54°	4·78°	8·20°	12·90°	16·52˙
	49°	55˙	58˙	69˙	103·5˙	125°	145°	168˙	199
	20·32˙	23·70˙	25·34˙	31·86˙	43·34˙	46·80˙	47·90°	48·30˙	45·16˙

Temp.	15°	24˙	25˙	26·5°	28˙	32°	39˙	43
aᵥ₁ ...	−24·82˙	−6·00˙	5·06˙	−3·34˙	−0·76˙	+5·10°	14·24˙	21·48
	56°	58˙	69	73˙	104°	125°	143°	169	199
	36·42°	37·48°	49·42˙	50·90˙	72·20˙	79·20˙	81·04°	81·90˙	76·16˙

Acetate of d-1-Naphthyl-n-hexylcarbinol.

Temp.	19·5˙	54˙	90˙	132°
D'₄	1·0266	1·0001	0·9699	0·9371

Temp.	21°	47˙	83°	104°	123°	151˙	18
aₚ	+24·56	29·90˙	34·58°	36·68˙	37·58˙	38·64˙	38·8

Temp.	21°	49˙	83°	104°	123°	158	18
aᵧₑₗₗₒw	+25·96˙	31·54˙	36·50˙	38·26°	39·68	40·58	59·7

Temp.	21˙	49˙	83˙	104°	123°	153	18
aₘᵣ	29·72˙	36·50˙	42·00	44·10°	45·66˙	46·90	46·4

Temp.	21°	49·5˙	83°	104°	123°	158	18
aᵥ₁	+54·88°	67·42°	78·30˙	82·18°	85·00˙	87·20	88·5

Propionate.

Temp.	20·5°	56°	94°	134°
D'₄	1·0144	0·9885	0·9574	0·9208

Temp.	24°	54°	68°	97°	123°	153˙	18
aₚ	+29·96°	35·32°	37·08°	39·88°	41·00°	41·40	43·2

Temp.	24°	52°	75°	96°	123°	152˙	18
aᵧₑₗₗₒw	+31·42°	36·58°	39·30°	41·80°	42·70°	43·34	45·5

Temp.	24°	52°	76°	96°	123°	152	18
aₘᵣ	+36·26°	42·46°	45·86°	48·04°	49·46°	50·24	49·8

Temp.	24°	51°	76°	96°	123°	152°	18
aᵥ₁	+67·80°	79·00°	86·10°	90·30°	92·96°	94·16˙	93·6

n-Butyrate.

	18°	61°	97°	134·5
	1·0066	0·9739	0·9459	0·9155

	20°	30°	60°	85°	105	121°	163	195
	27·12°	28·94°	32·78°	34·86°	35·92	36·28	36·76	36·42

	20°	57°	85°	105	121	163	195
	28·30°	34·26°	36·60°	37·78°	38·18	38·56	38·18
	32·70°	39·54°	42·50°	43·60°	44·34	44·60	44·02

	20°	56°	84°	105°	121	163	195°
	60·50°	73·70	79·20°	81·90	82·78	83·66	82·40

n-Valerate.

	20·5°	56·5°	93°	132°
	0·9956	0·9694	0·9410	0·9088

	23°	45°	65°	87°	119°	138	182°
	22·58°	25·68°	27·68	29·38°	30·72	31·40	30·90

	23°	47°	87°	120°	138	182
	23·68°	27·01°	30·74	32·26	32·56	32·32

	23°	47°	87	121	138°	182
	27·28°	31·22°	35·48	37·26°	37·66	37·38

	23°	47°	87°	122°	138	182
	50·70°	58·80°	66·42°	69·84	70·58°	70·08

n-Hexoate.

	19°	57°	97°	146°
	0·9897	0·9636	0·9285	0·8911

	20°	48°	60°	72°	107°	130	152	170°
	20·90°	24·36°	25·30°	25·90°	27·40	27·80	28·14	28·16

	20°	49°	58°	76°	109°	129	153	170
	22·12°	25·80°	26·46°	27·68°	29·16	29·38	29·70	29·71

n-Heptoate.

	18°	53·5°	97°	141	
....	0·9825	0·9584	0·9220	0·8874	
....	20°	56°	82°	114°	148°
....	+19·30°	22·66°	24·18°	24·84°	24·92
....	20°	53°	87°	116°	148°
....	+20·24°	23·66°	25·40°	26·04°	26·14
....	20°	52°	86°	117°	148°
....	+23·28	26·76	28·88	29·82°	30·00

n-Octoate.

	18°	55°	92°	144·5°
....	0·9806	0·9549	0·9263	0·8880

n-Octoate (continued).

Temp.	20°	44°	58°	69°	88°	120°	143	
a_D	20·70°	22·94°	23·84°	24·36°	24·80°	25·50°	25·84	

Temp.	20°	45°	68°	91°	118°	145	
a_{yellow}	21·66°	24·24°	25·80°	26·00°	26·76°	26·92	
a_{gr}	24·94°	27·88	29·84°	29·96°	30·74°	30·68	

Temp.	20°	45°	67°	90°	117°	143	
a_s	49·60	52·28°	55·74°	56·48°	57·60°	57·60	

n-Nonoate.

Temp. ...	17	59	95°	144·5°
D_4^t	0·9734	0·9442	0·9157	0·8800

Temp. ...	18	35°	77°	98°	136	
a_D	· 18·30°	20·20°	21·92°	22·40°	22·60	

Temp. ...	18	58°	71°	101°	136	
a_{yellow} ...	· 18·92°	22·00°	22·60°	23·24°	23·64	

Temp. ...	18	60	74°	101°	136	
a_{gr}	22·00	25·60	26·26°	27·00°	27·38	

n-Decoate.

Temp.	20·5°	58°	94°	132
D_4^t	0·9674	0·9410	0·9137	. 0·8812

Temp.	20°	56°	95°	135
a_D	+ 16·60°	19·00°	20·40°	20·78

Temp.	20°	49°	95°	135
a_{yellow}	+ 17·54°	19·38°	21·18°	21·60
a_{gr}	20·16°	22·46°	24·44°	25·00

n-Undecoate.

Temp.	20·5°	58°	94°	132
D_4^t	0·9605	0·9341	0·9075	0·8792

Temp.	20°	61°	94°	
a_D	+15·80°	18·36°	19·22°	
a_{yellow}	+16·42°	18·94°	19·84	
a_{gr}	+19·00°	21·74°	22·54	

Acetate of 1·1·Naphthylmethylcarbinol

Temp.	16°	64°	99°	138°
D_4^t	1·1071	1·0699	1·0380	1·0019

Temp.	27°	36°	56°	100°	136	160
a_D	−38·66°	41·84°	46·90°	54·80°	56·70	57·00

Temp.	19°	27°	36°	61°	78°	101	136
a_{gr}	−42·70°	47·02°	50·10°	58·32°	62·26°	66·84	68·76

Temp.	27°	34°	62°	76°	100°	136	160
a_{bl}	−87·30°	91·90°	110·30	115·30°	126·00°	129·66	130·2

a every case these esters were found to have undergone no
alteration during the heating in the polarimeter tube, whilst all
them when hydrolysed yielded samples of the carbinols of
tary power identical with that of the original preparations.

XLIX.—*Carboxylic Acids Derived from* cyclo*Butane*, cyclo*Pentane*, cyclo*Hexane*, *and* cyclo*Heptane*.

By LEONARD JAMES GOLDSWORTHY *and*
WILLIAM HENRY PERKIN, jun.

present investigation is one of a series which has been insti
d with the object of obtaining further evidence relating to the
parative readiness of formation and stability of cyclic struc-
s containing varying numbers of carbon atoms. Judging by the
b produced in analogous reactions, experience is roughly in
dance with Baeyer's "Spannungstheorie," and seems to indi-
that, in the *cyclo*propane, *cyclo*butane, *cyclo*pentane, and
hexane series, derivatives of *cyclo*propane are produced with
greatest difficulty, and that, whilst derivatives of *cyclo*butane
cyclohexane are much more readily obtained, the tendency to
cyclopentane derivatives is so pronounced that these are
s produced in quantitative yields, and not infrequently during
ens which might be expected to lead to the formation of
ring complexes. The evidence on this point, however, is often
lacting, since it has frequently been observed that, although
cyclic derivatives are obtained in very small yields, other
natives of the same ring seem to be produced under very similar
items with great readiness. Thus the yield of ethyl *cyclo*
ane 1-dicarboxylate (I) obtained when ethylene dibromide
with the sodium derivative of ethyl malonate is very small,
hes ethyl *cyclo*propane-1 : 2-dicarboxylate (II) is readily pre-

pared in good yield when ethylene dibromide is replaced by $\alpha\beta$-dibromopropionate in this interaction:

$$CH_2 \underset{CH_2}{\overset{C(CO_2Et)_2}{<}} \qquad CH_2 \underset{CH \cdot CO_2Et}{\overset{CH \cdot CO_2Et}{<}}$$
$$(I.) \qquad\qquad (II.)$$

Other similar cases have been observed, and one of the difficulties which arises is to distinguish between the effect on the yield of the reactivity of the interacting substances on the one hand and of the readiness of formation of the closed ring on the other.

It is clear that a useful generalisation cannot be formed until a much larger number of cyclic carboxylic acids and their derivatives have been prepared and investigated, and, in the present communication, we describe some new carboxylic acids derived from *cyclo*-butane, -pentane, -hexane, and -heptane. In the first place, we have prepared the *cis*- and *trans*-modifications of *butane*-1 : 2 : 3-*tricarboxylic acid,*

$$CH_2 \underset{CH(CO_2H)}{\overset{CH(CO_2H)}{<}} CH \cdot CO_2H,$$
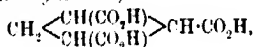
by causing ethyl $\alpha\beta$-dibromopropionate to react with the sodium derivative of ethyl ethanetetracarboxylate, when the reaction proceeds to the extent of about 50 per cent. in the required direction:

$$CO_2Et \cdot CHBr \atop CH_2Br \quad + \quad {N \cdot C(CO_2Et)_2 \atop NaC(CO_2Et)_2} \ = \ {CO_2Et \cdot CH-C(CO_2Et)_2 \atop CH_2 \cdot C(CO_2Et)_2} \ + \ N.$$

The product, after hydrolysis and elimination of carbon by heating at 190°, yields cis-cyclo*butane*-1 : 2 : 3-*tricarb*... (m. p. 141—143°), and this, when heated with hydrochlo... 180°, is converted into the *trans*-acid, which melts at 1...

In the *cyclo*pentane series the *cis*- and *trans*-modifications of 1 : 2 : 4-tricarboxylic acid **have** already been prepared fr disodium derivative of ethyl pentane-$\alpha\alpha\gamma\gamma\epsilon\epsilon$-hexacarboxylate action of iodine and subsequent hydrolysis and elimination of carbon dioxide:

$$C(CO_2Et)_2 \underset{CH_2 \cdot CNa(CO_2Et)_2}{\overset{CH_2 \cdot CNa(CO_2Et)_2}{<}} \rightarrow C(CO_2Et)_2 \underset{CH_2 \cdot C \cdot CO_2}{\overset{CH_2 \cdot C \cdot CO_2}{<}}$$
$$CO_2H \cdot CH \underset{CH_2 \cdot CH \cdot CO_2H}{\overset{CH_2 \cdot CH \cdot CO_2H}{<}}$$
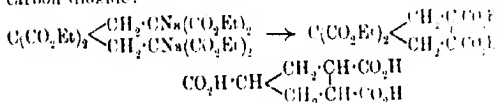
(Bottomley and Perkin, T., 1900, **77**, 296). We have succeeded in obtaining the same acids much more conveniently a much better yield by the action of ethyl $\alpha\beta$-dibromopro... the disodium derivative of ethyl propane-$\alpha\alpha\gamma\gamma$-tetra... (ethyl methylenedimalonate):

$$CNa(CO_2Et)_2 \cdot CH_2 \cdot CNa(CO_2Et)_2 \atop CH_2Br \cdot CHBr \cdot CO_2Et \quad \rightarrow \quad C(CO_2Et)_2 \underset{CH_2 \cdot CH}{\overset{CH_2 \cdot C}{<}}$$
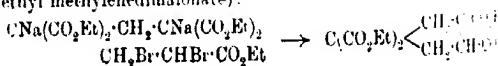
When the product of this interaction is hydrolysed, simultaneous elimination of one molecule of carbon dioxide takes place and a crystalline cyclopentanetetracarboxylic acid is formed. The crude acid decomposes at 180°, and yields a syrupy mass, from which pure cyclopentane-1:2:4-tricarboxylic acid is obtained by the action of hydrochloric acid at 190°. It melts at 127—130°, and is converted, by heating with acetic anhydride and subsequent distillation, into the anhydro-cis-acid:

$$CO_2H \cdot CH \underset{CH_2 \cdot CH \cdot CO}{\overset{CH_2 \cdot CH \cdot CO}{<}} O,$$
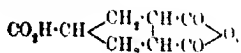
a highly characteristic derivative, which melts at 215—217°, and furnishes the cis-acid (m. p. 146—148°) on hydrolysis.

We next attempted the synthesis of cyclohexane 1:2:4 tricarboxylic acid (hexahydrotrimellitic acid),

$$CO_2H \cdot CH \underset{CH_2 \cdot CH(CO_2H)}{\overset{CH_2 \text{———} CH_2}{<}} CH \cdot CO_2H,$$
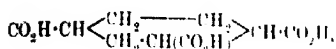
and which does not appear to have been previously described, and ultimately succeeded in the following manner. The disodium derivative of ethyl butanetetracarboxylate was caused to react with ethyl αβ-dibromopropionate, when decomposition takes place in the following manner:

$$\begin{array}{l} CNa(CO_2Et)_2 \cdot CH_2 \cdot CH_2 \cdot CNa(CO_2Et)_2 \\ \qquad CH_2Br \cdot CHBr \cdot CO_2Et \end{array} \longrightarrow$$

$$C(CO_2Et)_2 \underset{CH_2 \cdot CH(CO_2Et)}{\overset{CH_2 \text{———} CH_2}{<}} C(CO_2Et)_2 .$$
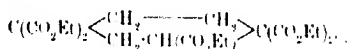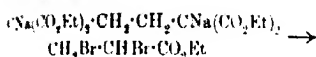
The ester thus produced yields, on hydrolysis and elimination of carbon dioxide, a mixture of stereoisomeric acids, from which, by heating with hydrochloric acid at 190°, trans cyclohexane-1:2:4-tricarboxylic acid was isolated, melting at 220—222°. When this acid was digested with acetic anhydride and the product distilled, most of it decomposed, but a small quantity of a distillate was obtained, which, on hydrolysis, yielded the cis-acid as a crystalline solid melting at 225°. It is remarkable that the cis- and trans-modifications of this acid should have almost identical melting points, and be so very similar in other properties that it was at first thought that they were identical.

However, a mixture of equal parts of the two preparations was found to soften at 198—200°, and to be almost completely melted at 205°, so that they cannot be identical, and there can be little doubt that they are the cis- and trans-modifications of cyclohexane-1:2:4-tricarboxylic acid.

Finally, we have succeeded in synthesising trans-cy̆c̆lŏhěp̆tanĕ
1 : 2 : 4-tricarboxylic acid :

$$CO_2H \cdot CH < ^{CH_2-CH_2-CH_2}_{CH_2 \cdot CH(CO_2H)} > CH \cdot CO_2H$$
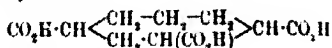
one of the few derivatives of cycloheptane which have . . . .
obtained. For the purpose of this synthesis, the disŏ̆ȟă̆n̆ ̆v̆
ative of ethyl pentane-αααε-tetracarboxylate was digested w̆h ̆m̆r̆
αβ-dibromopropionate when a complicated reaction tŏŏk̆ p̆l̆ăc̆ẽ̆
an ester, evidently ethyl cyclopentane-1 : 1 : 2 : 4 : 4-pentăc̆ă̆r̆. n̆x̆
was produced in small quantity according to the equatiŏṅ ̆

$$CNa(CO_2Et)_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CNa(CO_2Et)_2 \longrightarrow$$
$$CH_2Br \cdot CHBr \cdot CO_2Et$$
$$C(CO_2Et)_2 < ^{CH_2-CH_2-CH_2}_{CH_2 \cdot CH(CO_2Et)} > \cdots \cdots$$
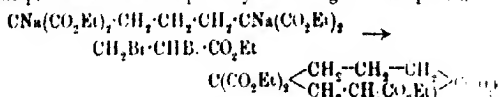
When the product of this interaction was hydrolysed, t̆ḣ̆ẽ̆ ̆̆
acid mixture heated at 200° and then esterified, it yĭĕl̆d̆ ̆ă ̆̆
quantity of ethyl cycloheptane-1 : 2 : 4-tricarboxylate . . ĭ̆
212—215°/30 mm.).

On hydrolysis a syrupy mixture of stereoisomeric ăc̆id̆s̆ ̆v̆ăs̆
was obtained, from which, by heating with hydrochloric ăc̆ĭ̆d̆
190°, trans-cycloheptane-1 : 2 : 4-tricarboxylic acid was ĭs̆ŏ̆l̆ă ̆ ̆
ing at 198—200°.

Apparently there is little tendency in the direction of t̆ḣẽ̆ ̆̆ ̆
tion of the cycloheptane ring, since the yield of the ăb̆ŏ̆v̆ĕ ̆ăc̆ĭd̆s̆
so small that we were unable to examine it at all c̆ŏm̆p̆l̆ẽ̆t̆
Further experiments, which are in progress, will show whĕt̆h̆ĕr ̆t̆
ring and also the cyclo-octane and still larger rings are ăl̆s̆ŏ̆
produced with more difficulty than the simpler rings c̆ŏn̆t̆ăĭ ̆
three, four, five, and six carbon atoms.

EXPERIMENTAL.

Preparation of Ethyl αβ-Dibromopropionate, $CH_2Br \cdot CHBr \cdot CO_2Et$

During the course of this and other investigations, l̆ăr̆ğĕ ̆̆
ties of ethyl αβ-dibromopropionate were required, and, as t̆h̆ĕ ̆̆
charged for this ester is prohibitive, we have made a s̆ĕr̆ĭ̆ĕs̆
comparative experiments on the best conditions for its p̆r̆ẽ̆p̆ă̆r̆̆
and find that the following process works well. Allyl ăl̆c̆ŏh̆ŏl̆*
(180 grams or 210 c.c.) is mixed with an equal volume of c̆h̆l̆ŏ̆r̆ŏ̆
form (or carbon disulphide), the solution cooled in ice ăn̆d̆ ̆ĭs̆

---

* Crude commercial allyl alcohol contains a large amount of water, ăn̆d̆ ̆ĭf̆ ̆ĭt̆ ̆ĭs̆
used as the starting-point, it is shaken with potassium carbonate as l̆ŏ̆n̆ğ ̆ăs̆ ̆ĭt̆
dissolved, the aqueous layer run off and the alcohol dehydrated w̆ĭt̆ḣ̆ ̆ă ̆f̆r̆ẽ̆s̆
quantity of potassium carbonate. It is then fractionated with an ĕf̆f̆ĭc̆ĭĕn̆t̆ ̆ ̆
the portion distilling at 95—98° was collected for use in the above p̆r̆ŏ̆c̆ĕs̆s̆

the bromine (496 grams or 156 c.c.) is gradually added, care being taken that the temperature remains below 5°. The chloro- is then removed by distillation from the water-bath under reduced pressure, and the residual crude dibromopropyl alcohol need not be fractionated, but can be directly oxidised to αβ dibromo- propionic acid. The crude dibromo-alcohol (150 grams) is mixed with ordinary concentrated nitric acid (210 grams or 140 c.c.) and fuming nitric acid (90 grams or 60 c.c. of D 1.5) in a capacious flask provided with a ground-in condenser and placed in water, and the water is then very gradually heated. As soon as the initial first reaction has subsided, the water is raised to the boiling point and maintained at that for seven hours; the product is then left overnight in the ice-chest to cool, when the dibromopropionic acid usually crystallises, but, if not, the heating is continued and the mass seeded. The acid is collected on a Buchner funnel without filter paper, drained on porous porcelain, and a further quantity is obtained by concentrating the mother liquors, so that the yield is about 75 per cent. of that theoretically possible. In order to obtain the ethyl ester, the acid is dissolved in one and a half times its own weight of a 10 per cent. solution of sulphuric acid in alcohol and heated on the water-bath for six hours. Water is then added, the heavy ester extracted with ether, the ethereal solution washed first with dilute sodium carbonate, then with water, dried, and the ether distilled off. The residual ethyl αβ di- bromopropionate distils almost completely at 140—150° 165 mm., and this was the material used in the following experiments.

For cis *and* trans-cyclo*Butane* 1 : 2 : 3 *tricarboxylic Acids.*

$$CH_2 <^{CH(CO_2H)}_{CH(CO_2H)} > CH \cdot CO_2H.$$
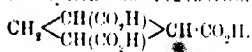
In order to obtain these acids, the first step was the synthesis of ethyl cyclobutane-1 : 1 : 2 : 2 : 3-pentacarboxylate (p. 2666), and this was accomplished in the following way: Ethyl ethanetetracarb- oxylate (31 grams) was mixed with a little alcohol, and then with a piece of sodium (4.6 grams) in alcohol (100 c.c.), and, after standing for a few minutes until the whole of the ester had passed into solution, ethyl αβ-dibromopropionate (27 grams) was gradually added. In a short time the mixture became warm, copious pre- cipitation of sodium bromide took place, and the process was com- pleted by heating in a soda-water bottle in boiling water for four hours. The product was mixed with water, extracted with ether, the ethereal solution washed well, dried, and the ether distilled off.

The alcohol used in all these experiments was carefully dehydrated by distillation over lime and then over calcium.

The crude ester which appears to distil at about 230° ... ... not be purified before conversion into *cyclo*butanetricarbo... ... but is at once hydrolysed by boiling with 50 per cent. ... 25 per cent. methyl-alcoholic potassium hydroxide for four ...

Water is then added, the product evaporated until ... from methyl alcohol, the solution is then acidified with con... concentrated hydrochloric acid, evaporated to dryness ... residue extracted with ether in a Soxhlet apparatus. After ... ling off the ether, crude *cyclo*butanepentacarboxylic acid re... a slightly brown, viscid syrup, and this is heated in an oil ... 190° for one hour, when the evolution of carbon dioxide ... ceased. The acid which remains does not readily crystal... therefore purified by conversion into the ester which is ... boiling the acid with ten times its weight of 10 per cent. ... sulphuric acid in a reflux apparatus for seven hours. ... is diluted with water, extracted with ether, the ethereal ... washed well with sodium carbonate, dried, and evaporated ... residue fractionated under 40 mm. pressure. A small qua... oil passes over below 190°, and probably contains ethyl ... then almost the whole of the remainder distils at 190 ... refractionation, pure *ethyl* cis-*cyclobutane*-1:2:3-*tricarb*... obtained as a colourless oil boiling at 195—197°/40 mm.

0·2246 gave 0·4714 CO_2 and 0·1540 H_2O. $C = 57·2$; H ...

$C_{15}H_{20}O_6$ requires $C = 57·3$; $H = 7·3$ per cent.

In the preparation of the tricarboxylic acid, the ester ... at 190 –205°/40 mm. was hydrolysed by boiling with ... 25 per cent. methyl-alcoholic potassium hydroxide for four ... Water was then added, the solution evaporated until ... from methyl alcohol, mixed with excess of hydrochloric ... porated, and the dry residue extracted with ether in ... apparatus. The ethereal solution deposited, after boiling ... ether, a solid acid, which was left in contact with porous ... and then recrystallised from concentrated hydrochloric ...

0·1410 gave 0·2332 CO_2 and 0·0592 H_2O. $C = 45·1$; H ...

$C_7H_8O_6$ requires $C = 44·7$; $H = 4·3$ per cent.

On titration, 0·1226 required 0·0772 NaOH for neutrali... whereas this amount of a tribasic acid, $C_7H_8O_6$, should ... 0·0782 NaOH.

cis-*cycloButane*-1:2:3-*tricarboxylic acid* melts at 141 ... is readily soluble in water or alcohol, but rather sparing... cold concentrated hydrochloric acid.

In order to obtain the *trans*-modification, the cis acid ... was heated with concentrated hydrochloric acid (15 c.c.) ... tube at 180° for two hours. After diluting with water and ...

x a trace of carbonaceous matter, the solution was concentrated,
x on standing over solid potassium hydroxide, a hard, glassy,
xlline mass, consisting of flat, glistening plates, gradually
xrated:

x31 gave 0·1699 CO_2 and 0·0411 H_2O. C 44·9; H 4·4.

$C_7H_8O_6$ requires C = 44·7; H 4·2 per cent.

x titration, 0·3500 neutralised 0·2236 NaOH, whereas this
xxxt of a tribasic acid, $C_7H_8O_6$, should neutralise 0·2234 NaOH.
xxxscyclo*Butane*-1:2:3-*tricarboxylic acid* melts at 168 170°,
x readily soluble in water, but sparingly so in concentrated
xxxhloric acid. The solution of the acid in excess of ammonia
x when boiled with barium chloride, a very sparingly soluble
xxx salt, and the *cis*-acid behaves in a similar manner. Both
x are oxidised with difficulty, even when their alkaline solutions
xxxed with permanganate.

x Trianilide of the trans-*Acid*. In order to prepare this deriv-
x the pure *trans*-acid was heated with thionyl chloride in a
xx tube at 100° for an hour; the product was then evaporated,
x residual syrup dissolved in benzene. Aniline was added
xxxess, and, as soon as the vigorous action had subsided, the
xxxne was evaporated, the mass treated with dilute hydrochloric
x and the precipitate collected and drained on porous porcelain.
x trianilide of trans-cyclo*butane*-1:2:3 *tricarboxylic acid* melts
xx, and separates from alcohol, in which it is sparingly soluble,
x voluminous, almost gelatinous, mass of needles. For analysis
xx recrystallised by dissolving in acetone and adding benzene;
xxetone was then distilled off, and the solution set aside, when
xxxbstance separated as a crystalline crust of needles:

xx9 gave 21·5 c.c. N_2 at 17° and 763 mm. N 10·2.

$C_{25}H_{23}O_3N_3$ requires N = 10·2 per cent.

xxder to make sure that transformation of the *trans*-acid into
xxxodification had not taken place during the heating with
xx chloride, some of the syrupy product of this action was
xxxposed by boiling with water and the acid recrystallised, when
xxxed at 168—170°.

The cis *and* trans-cyclo*Pentane*-1:2:4-*tricarboxylic Acids,*

$$CO_2H\cdot CH \begin{cases} CH_2\cdot CH\cdot CO_2H \\ CH_2\cdot CH\cdot CO_2H \end{cases}$$
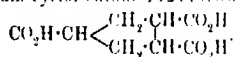
x ethyl *cyclo*pentane-1:1:2:4:4-pentacarboxylate employed in
x synthesis of these acids was obtained under the following
xxxons.

Exxl methylenedimalonate, $(CO_2Et)_2CH\cdot CH_2\cdot CH(CO_2Et)_2$ (33·2

grams), dissolved in alcohol (50 c.c.) was added to a c... ...
sodium (4·6 grams) in alcohol (100 c.c.), and, after a ...
the disodium derivative was mixed with ethyl αβ-dibr... ...
(26 grams), when gradual rise of temperature, follow... ...
ous action, set in, and sodium bromide separated. 1 ...
was completed by heating for three hours in a soda w...
the product was diluted with water, extracted with eth...
washing well, drying, and evaporating off the ether, th...
was distilled, when almost the whole quantity pass...
226—240°/15 mm., and, on redistillation, the boiling...
ethyl *cyclo*pentanepentacarboxylate was observed ...
234—236°/15 mm. The ester was hydrolysed in th...
by boiling with excess of 25 per cent. methyl-alcoh...
hydroxide for four hours, the product was diluted ...
evaporated until free from methyl alcohol, acidified, ...
ated, and the mass extracted with ether in a Soxhle...
When the ethereal solution was evaporated, a ...
remained, which became partly solid while still on th...
This was stirred with concentrated hydrochloric acid, a...
powder which separated was collected, washed with ...
acid, left in contact with porous porcelain in a vacuu...
and then analysed:

0·1670 gave 0·2768 CO_2 and 0·0644 H_2O. C=43·7 ; H
$C_5H_6O_8$ requires C = 43·9 ; H = 4·0 per cent.

It is obvious that during the hydrolysis under the ...
tions one molecule of carbon dioxide had been eliminat...
the above acid is *cyclopentane*-1:2:2:4-*tetracarboxyli*...

$$CO_2H \cdot CH < \frac{CH_2 \cdot C(CO_2H)_2}{CH_2 \cdot CH \cdot CO_2H}$$
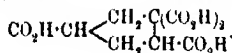
Ethyl cyclo*Pentane*-1:2:4-*tricarboxylate*, $C_5H_7(CO_2H)$...
order to prepare this ester the crude product of the ...
ethyl *cyclo*pentanepentacarboxylate was heated at 19...
hour, when a glassy mass remained, which did not crys...
was converted into the ester by heating with alcohol ...
acid in the usual manner (p. 2670), and the pure subst...
at 205—210°/40 mm. :

0·1938 gave 0·4186 CO_2 and 0·1360 H_2O. C=58·9 ; H
$C_{14}H_{22}O_6$ requires C = 58·7 ; H = 7·8 per cent.

The corresponding trimethyl ester, $C_5H_7(CO_2Me)$ ...
viously obtained (T., 1900, **77**, 303), and distilled at ...
12 mm. The pure triethyl ester was hydrolysed w...
alcoholic potassium hydroxide in the usual manner. ...
removal of the methyl alcohol, acidifying and ev...

ness, the mass was extracted with ether in a Soxhlet apparatus. ... evaporation, the ethereal solution deposited a syrup, which, ... rubbed with concentrated hydrochloric acid, crystallised, and ... solid mass, after washing with hydrochloric acid and drying on ... porcelain, melted indefinitely at 115—125°, and was apparently a mixture of the *cis*- and *trans*-modifications of *cyclo*pentane-... tricarboxylic acid. In order to demonstrate this, half of the ... mass was heated with hydrochloric acid in a sealed tube at ... for four hours. The product was diluted with water, filtered ... a small amount of carbonaceous matter, and evaporated to ... ness. It was then dissolved in water, digested with animal ... and again evaporated. When the syrupy residue was ... with concentrated hydrochloric acid, it crystallised with ... difficulty (compare T., 1900, **77**, 304), and the solid mass, after ... with porous porcelain and recrystallisation from hydro-... acid, melted at 129—130°, and consisted of *trans*-cyclo-... ane-1:2:4-tricarboxylic acid:

... gave 0·2224 CO_2 and 0·0568 H_2O. C = 47·9; H = 5·0.

$C_9H_{10}O_6$ requires C = 47·5; H = 4·9 per cent.

... titration 0·1528 neutralised 0·0880 NaOH, whereas this ... of a tribasic acid, $C_9H_{10}O_6$, should neutralise 0·0907 NaOH.

*cycloPentane-*1:2:4-*tricarboxylic Acid.* This modification ... obtained by heating the crude mixture of acids melting at ... 125° (see above) with acetic anhydride for an hour, and then ... ching the product, when anhydro-*cis*-*cyclo*pentanetricarboxylic ... solidified in the neck of the retort. After recrystallisation from ... nature of acetone and chloroform, this substance melted at ... 217°, as stated by Bottomley and Perkin (*loc. cit.*, p. 305). ... solution of the anhydro-acid in water deposited, on concentra-... colourless crystals of *cis*-*cyclo*pentane-1:2:4-tricarboxylic acid, ... at 146—148°.

cis- *and* trans-cyclo*Hexane*-1:2:4-*tricarboxylic Acids* (*Hexahydrotrimellitic Acids*).

$$CO_2H \cdot CH \begin{matrix} CH_2 \text{-----} CH_2 \\ CH_2 \cdot CH(CO_2H) \end{matrix} CH \cdot CO_2H.$$

The ethyl butanetetracarboxylate,

$$CH(CO_2Et)_2 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2,$$
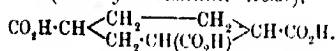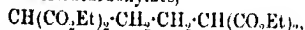
... used for these experiments was prepared by the process ... described by Perkin (T., 1894, **65**, 578). This ester (34·6 grams), ... dissolved in an equal weight of alcohol, was mixed with a solution ... sodium (4·6 grams) in alcohol (100 c.c.) and then with ethyl ... bromopropionate (26 grams), when, on setting aside, the

mixture gradually became quite hot. After heating for [...] in a soda-water bottle in boiling water, water was added [...] ester extracted with ether, and, since it decomposed on [...] it was at once hydrolysed by boiling with excess of [...] per [...] methyl-alcoholic potassium hydroxide in the usual manner.

Water was then added, the methyl alcohol carefully removed [...] the water-bath, the product acidified with excess of hydro[...] acid, evaporated to dryness, and extracted in a Soxhlet appa[...] with ether.

On evaporation, the ethereal extract deposited a syrup [...] partly solidified, and this was heated at 190° for half an [...] syrupy residue being then esterified by boiling with [...] sulphuric acid and the ester fractionated (compare p. [...] cyclo*hexane*-1:2:4-*tricarboxylate* was thus obtained as [...] oil, which distilled at about 207°/30 mm.:

0·1893 gave 0·4142 CO_2 and 0·1374 H_2O. C=59·5, H [...]

$C_{15}H_{24}O_6$ requires C=60·0; H=8·0 per cent.

This ester was hydrolysed by boiling with excess of 20 per [...] methyl-alcoholic potassium hydroxide for four hours, and [...] the methyl alcohol had been completely removed, hydroch[...] was added, the whole evaporated to dryness, and extracted [...] ether in a Soxhlet apparatus.

The syrup which remained on distilling off the ether, only [...] solidified when it was rubbed with hydrochloric acid, and then had an indefinite melting point, obviously consisting of two or [...] stereoisomeric modifications. In order to isolate one definite [...] fication (*trans*), the whole was heated with concentrated [...] chloric acid in a sealed tube at 190° for four hours, the pro[...] was diluted with water, filtered from a small amount [...] aceous matter, decolourised with animal charcoal, and eva[...] to dryness, during which the acid commenced to separate in [...] less crystals. After remaining in the ice-chest for two day[...] crystals were collected, dissolved in ether, filtered from a tra[...] inorganic matter, and the ether removed, when a solid left [...] which was crystallised from hydrochloric acid:

0·1786 gave 0·3304 CO_2 and 0·0948 H_2O. C=50·4; H [...]

$C_9H_{12}O_6$ requires C=50·0; H=5·6 per cent.

On titration 0·1526 required for neutralisation 0·0[...] N[...] whereas this amount of a tribasic acid, $C_9H_{12}O_6$, neutralises [...] NaOH.

trans-cyclo*Hexane*-1:2:4-*tricarboxylic acid* is rather spa[...] soluble in cold, but readily so in hot water, and has a [...] tendency to form supersaturated solutions, which only give [...]

pent the acid as a hard, opaque, crystalline crust. It melts at
mal 220—222° to a colourless, viscid syrup, but the exact point is
kault to observe.

trans-cycloHexane-1:2:4-tricarboxylic Acid.—In order to obtain
a acid. the pure trans-acid (2 grams) was mixed with acetic
ydride (5 c.c.) in a test-tube, and gently boiled by means of a
paraffin-acid bath for one hour; the temperature was then raised,
2 the excess of acetic anhydride distilled off. The test tube was
was cut, and the whole heated as rapidly as possible over a
r flame, when there was much decomposition and a voluminous
carbonaceous mass remained.

The small quantity of brown distillate, which partly solidified
keeping, was boiled with much water, filtered from a little tar,
cleansed with animal charcoal, and then evaporated to a small
and mixed with an equal volume of concentrated hydrochloric
. On remaining in the ice-chest a crystalline crust gradually
mass, and this was collected and crystallised from water, in
which it is rather sparingly soluble in the cold, and from which
or acid separated as a crust of colourless, warty masses, which
a quite different appearance from the crystals of the trans-
.

452 gave 0·2630 CO₂ and 0·0752 H₂O. C = 50·2; H = 5·8.

$C_9H_{12}O_6$ requires C = 50·0; H = 5·6 per cent.

titration 0·1405 required 0·0764 NaOH for neutralisation,
cross this amount of a tribasic acid, $C_9H_{12}O_6$, neutralises 0·0780
OH

cycloHexane-1:2:4-tricarboxylic acid softens at 218°, melts
, and, when it is mixed with an equal amount of the
esterification, the mixture softens very much at 198—200 ,
is almost completely melted at 208° (compare p. 2667).

trans-cycloHeptane-1:2:4-tricarboxylic Acid,

$$CO_2H \cdot CH < ^{CH_2-CH_2-CH_2}_{CH_2 \cdot CH(CO_2H)} > CH \cdot CO_2H.$$
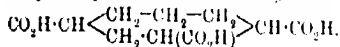
investigation of this interesting acid has been rendered diffi
owing to the small yield which is produced by the following
and it has not been found possible to obtain better results
varying these conditions. Ethyl cycloheptane-1:1:2:4:4-penta-
carboxylate (p. 2668) was first prepared by mixing 36 grams of
pentanetetracarboxylate,

$$CH(CO_2Et)_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2$$
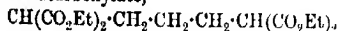
Perkin, T., 1887, **41**, 240), first with a solution of sodium ethoxide
de by dissolving sodium (4·6 grams) in alcohol (100 c.c.), and

then with ethyl $\alpha\beta$-dibromopropionate (26 grams), and, after the
initial somewhat vigorous action had subsided, the whole was heated
in a soda-water bottle in boiling water for four hours. The product
was isolated by adding water and extracting with ether, and
hydrolysed in the usual manner (p. 2670), the crude, dark brown,
syrupy polybasic acid being heated at 200° for an hour, and the
residue esterified by boiling with alcohol and sulphuric acid. On
distillation a considerable amount of ethyl pimelate,

$$CO_2Et \cdot [CH_2]_5 \cdot CO_2Et,$$
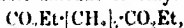
passed over at about 190—195°/100 mm., and then ethyl
*cyclo*heptanetricarboxylate distilled at 200—230°/30 mm., leaving
a considerable dark coloured residue in the distilling flask. The
crude tricarboxylic ester was redistilled, and the fraction boiling
at 212—215°/30 mm. analysed, but the yield obtained was only
7 grams, or 8 per cent. of that theoretically possible.

0·1960 gave 0·4390 CO_2 and 0·1504 H_2O. C = 61·1, H ··

$C_{16}H_{26}O_6$ requires C = 61·1; H = 8·3 per cent.

This ester was hydrolysed by boiling with methyl- or
potassium hydroxide in the usual manner, and, after removal of the
alcohol, excess of hydrochloric acid was added, the whole evaporated
to dryness, and extracted with ether in a Soxhlet apparatus. The
residue from the ether was a syrup, which could not be induced to
crystallise, and was doubtless a mixture of stereoisomerides. It
was heated with hydrochloric acid in a sealed tube at 150° for
four hours, the product diluted with water, filtered from a small
amount of carbonaceous matter, and the hydrochloric acid removed
by evaporation. The residue was dissolved in water, boiled with
animal charcoal, and again evaporated, when a viscous, colourless
syrup was obtained, which, on rubbing, almost completely solidified.
After contact with porous porcelain, the acid separated from hydro-
chloric acid in hard, nodular masses:

0·1100 gave 0·2106 CO_2 and 0·0623 H_2O. C = 52·2; H = 6·3

$C_{10}H_{14}O_6$ requires C = 52·2; H = 6·1 per cent.

On titration 0·0488 required 0·0250 NaOH for neutralisation,
whereas this amount of a tribasic acid, $C_{10}H_{14}O_6$, should require
0·0254 NaOH.

trans-cyclo*Heptane*-1 : 2 : 4-*tricarboxylic acid* melts at 149°
and is readily soluble in water. Unfortunately the amount of
material available was not sufficient for the preparation of the
cis-acid.

THE UNIVERSITY MUSEUM,
OXFORD.

L.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part X. The Optical Dispersive Power of Tetrahydro-2-naphthol and its Esters.*

By JOSEPH KENYON and ROBERT HOWSON PICKARD.

ᵢₜ been shown in **Parts VI and IX** (this vol., pp. 1117 and ₜₕₐₜ the optically **active** 1-naphthylalkylcarbinols of the ₐₗ formula $C_{10}H_7\cdot CH(OH)\cdot R$ have complex dispersive powers ₜₑₘₚₑᵣₐₜᵤᵣₑₛ **up to** those far removed from their melting ₜ Thus **the methyl** member of the series has a complex dis-ᵥₑ power **at all temperatures** up to about 160° and the corre-ₛₚₒₙₓ ₙ-**hexyl homologue** up to about 180°, above which limiting ₑᵣₐₜᵤᵣₑₛ **the rotations** of each obey the law of simple dispersive ₜ ₐₛ **expressed** by the Drude equation with one term, ᵢ ᴬᶜᴵ. It is **further** of interest to note that in the super-ₛ ₛₜₐₜₑ at **a few degrees** below the melting points of these ₜₐₙₔₛ their temperature-rotation curves for sodium-yellow to ₓᵣᵧ violet light, which are perfectly regular throughout, exhibit ₙ of so-called anomalous dispersion.

ₛₛ been **suggested** (*loc. cit.*) that below these limiting tem-ₐᵣₑₛ the apparently homogeneous carbinols are really mixtures ₛ ᵢₛₒₘₑᵣᵢₔₑₛ having rotatory powers of opposite sign, and ₙₖ ᵢₙ dispersive power. The further suggestion that the ₘₐₙ ᵢₛ due **to a different** disposition of the valencies in the ₐᵧₗ radicle (the two forms being of the nature of *ar-* and ᵢₐₜᵢᵥₑₛ) makes it desirable to consider the dispersive power ᵣₜ compounds containing either the naphthyl radicle or other ₜ ₖₗₒₛₑₗy **related to it.**

ₐₗᵧ ᵢₙ **Part III** (T., 1912, **101**, 1427) the preparation and ᵢ the optical **properties** of both dextro- and lævo-rotatory ᵢᵧₔᵣₒ-2-naphthol have been described, but unfortunately ₜₔ measurements were confined to light of one wave-length ᴬᶜᶜᵒᵣᵈⁱⁿˡⁱⁿgly, the work described there has been partly ᵦₑₔ and the **results confirmed** and extended. It has now been ᵣ ₜₕₐₜ the **temperature-rotation** curves of *ar*-tetrahydro-2-ₐₒₗ ᵢₙ the **fused state** from a temperature of about 120° down ᵢᵣₑᵢₜᵢₙg **point at 50°,** and beyond in the supercooled state to ₕₐₜₕ 15°, are **perfectly regular** and smooth. The rotations ᵦₑₔ ᵢₙ the **homogeneous** state up to 120°, as also in various ₖₜₛ obey the **law** of simple dispersive power, but above 120°

 L ᶜⱽ

8 M

FIG. 1.

CHARACTERISTIC DIAGRAM
for
α-Tetrahydro-2-naphthol and some
of its derivatives.
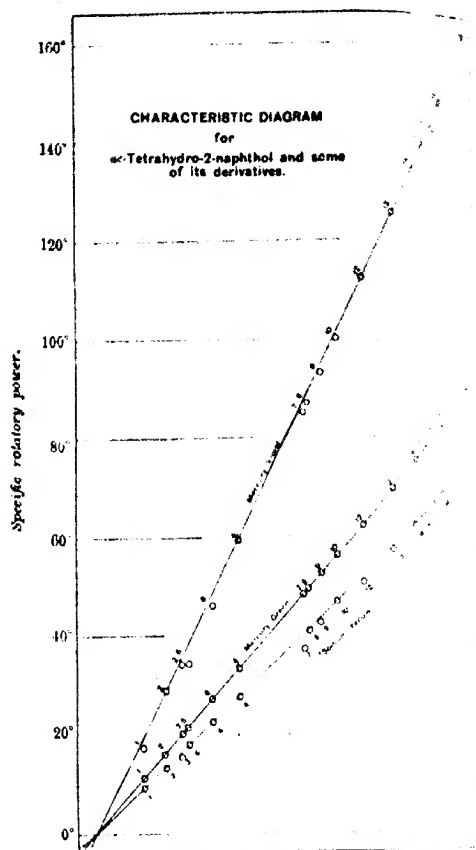
Points marked 1 to 4 correspond with the rotations of the hydrogen [is] at 5 per cent. concentration in ethyl alcohol, chloroform, pyridine [and] respectively, points 5 and 6 with ethyl-alcoholic solutions of the [ ] potassium salts, points 7, 9 and 10 with the rotations of the valera[ ] homogeneous state at 200°, 100° and 20° respectively, and points [ ] solutions of the valerate in chloroform and carbon disulphide. Points [ ] to 17 refer to the rotations of the tetrahydronaphthol in the homogeneous [ ] 200°, at 140°, dissolved in carbon disulphide and in chloroform, [and] a [ ] homogeneous state at 60° and 20° respectively. It will be noticed [ ] marked 1, 3, 5, 6, 7 and 12 do not fit on the lines of the diagram.

ispersive power becomes complex. Of this phenomenon there
s not seem to be any simple explanation, but the properties of
reduced compound are in marked contrast to those of the
phthylalkylcarbinols. The *n*-valeric ester in the homogeneous
e at 20° and in solution and the hydrogen phthalate when
dred in benzene or chloroform also exhibit rotations, which
ar to conform to the law of simple dispersive power. The
rate, however, in the homogeneous state at higher temperatures,
ters of hydrogen phthalate in alcohol or pyridine, and aqueous
alcoholic solutions of the sodium or potassium salt of the latter
r all show complex dispersive power.

e alternative method of plotting such rotations by means of a
aracteristic diagram" brings out these relations in a striking
ner. Thus the diagram (Fig. 1), which is constructed in the
l manner, using the rotations for mercury-green light as a
rence line, only correlates those rotations of the substances just
tioned, which conform to the law of simple dispersive power.
not surprising that the diagram fails to correlate the rotations
the valerate in the homogeneous state at higher temperatures,
not only has the *ac*-tetrahydro-2-naphthol then a complex dis-
ive power, but also, as has been repeatedly shown, an esterified
clylic group exhibits complex dispersive power at high tem-
tures. Assuming that dynamic isomerism is the underlying
e of the complex dispersive power exhibited by a colourless
pound of simple chemical constitution (containing only one
metric carbon atom), it may be stated generally that in cases
complex dispersive power is exhibited at all temperatures the
pound will contain more than one possible centre of dynamic
erism. Illustrations of this general statement can be seen in
esters of the naphthylalkylcarbinols and of *ac*-tetrahydro-2-
thol. whilst each of the substances mentioned above as showing
et dispersive power when dissolved in certain solvents con-
when so dissolved, two possible centres of dynamic isomerism,
the observed rotations cannot be correlated on the characteristic
am (Fig. 1). However, the rotations shown by aqueous solu-
at various concentrations of sodium *ac*-tetrahydro-2-naphthyl
late can be correlated on another diagram (Fig. 2) specially
for these, and permit the inference that there is some relation
en them.

tention has already been drawn in this series of investigations
e danger of basing conclusions on the values of any one disper-
ratio. A good example of this danger is to be seen in the
tion ratios of the substances named in tables I and II. It
be noted that in the homogeneous state the ratio for mercury-

violet/green remains constant, but that for mercury-violet sodium yellow tends constantly to increase. This is well brought out in the diagram (Fig. 1), where the lines for violet, green and yellow

FIG. 2.

CHARACTERISTIC DIAGRAM
for
Sodium *l*-*ac*-tetrahydro-2-naphthyl
phthalate in aqueous solutions.
(1) 2·0 per cent. solution
(2) 4·2 ,, ,,
(3) 6·1 ,, ,,
(4) 8·0 ,, ,,
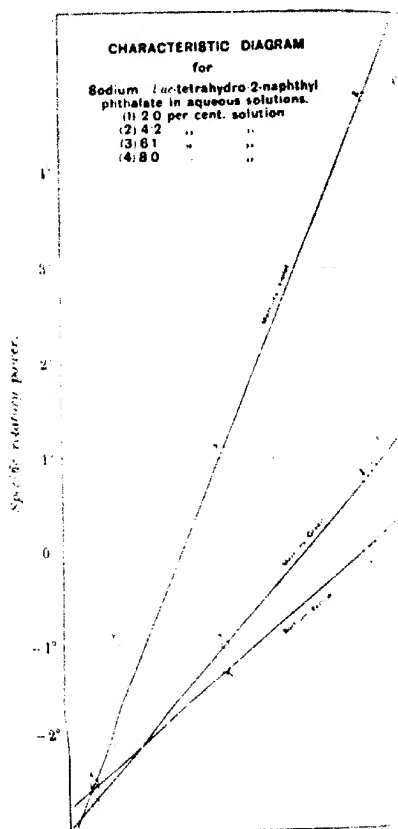
intersect at zero. When the green is used as a reference the rotation values for violet and green all lie approximately two lines, so that the dispersion ratio is constant, but in the where complex dispersive power (see, for example, points

TABLE 1

Rotatory Powers at Different Temperatures.

d-ac-Tetrahydro-2-naphthol.

Temp.	Density D.	$[\alpha]_r$	$[\alpha]_{gr}$	$[\alpha]_r$	$[M]_r$	$[M]_{gr}$	$[M]_r$	Mercury	Hg.../Na...
20°	1·0010	+75·68	+90·26	+162·16	+112·0°	+133·6°	+240·0°	1·797	2·142
40	1·0760	71·85	86·72	155·51	106·4	128·3	230·2	1·793	2·164
60	1·0590	68·35	82·62	148·94	101·2	122·3	220·5	1·793	2·170
80	1·0431	65·36	79·16	142·05	96·7	117·1	210·3	1·796	2·174
100	1·0275	62·56	75·39	135·65	92·6	111·6	200·8	1·790	2·169
120	1·0121	59·94	72·33	130·13	88·7	107·0	192·6	1·799	2·171
140	0·9965	57·50	69·82	125·88	85·1	103·4	186·3	1·803	2·190
160	0·9790	55·26	67·36	121·04	81·8	99·1	179·2	1·797	2·191
180	0·9630	52·96	64·66	116·16	78·4	95·7	177·9	1·796	2·193
200	0·9470	50·86	62·45	112·15	75·3	92·5	164·0	1·795	2·205

l-ac-Tetrahydro-2-naphthyl n-Valerate.

Temp.	Density D.	$[\alpha]_r$	$[\alpha]_r$	$[\alpha]_r$	$[M]_r$	$[M]_r$	$[M]_r$	Mercury	Hg.../Na...
20°	1·0284	−46·80	−54·23	−99·97	−108·6	−130·5	−231·9	1·774	2·135
40	1·0140	45·77	53·51	98·40	106·2	128·3	226·2	1·774	2·150
60	0·9995	44·71	54·13	96·74	103·7	126·3	224·7	1·771	2·166
80	0·9853	43·24	53·30	95·13	103·2	124·1	220·7	1·774	2·181
100	0·9709	42·49	52·32	93·40	98·6	121·8	215·5	1·775	2·199
120	0·9565	41·99	51·54	91·60	95·8	119·0	212·6	1·776	2·216
140	0·9421	40·65	54·55	89·80	92·9	117·3	204·4	1·776	2·245
160	0·9276	38·72	45·55	87·96	90·0	114·3	204·1	1·776	2·265
180	0·9133	35·43	48·45	85·96	86·4	112·1	199·5	1·774	2·297

TABLE II.

d-ac-Tetrahydro-2-naphthol.

Solvent	Length of observa-tion tube, cm.	Weight of substance dissolved, grams.	a_{μ}	a_{γ}	a_{β}	$[a]_{\mu}$	$[a]_{\gamma}$	$[a]_{\beta}$	$[M]_{\mu}$	$[M]_{\gamma}$	$[M]_{\beta}$	Hg (violet)	Mercury yellow / Sodium yellow
												Dispersion ratios	
Pyridine	22	1·0163	+8·49°	+10·23°	+18·40°	+75·97°	+91·54°	+164·6°	+112·4°	+135·5°	+243·6°	1·799	2·167
Ethyl alcohol	20	1·0313	7·79	9·37	16·63	75·56	90·88	161·4	111·9	134·5	238·8	1·775	2·135
Chloroform ...	22	0·9968	7·58	8·85	15·70	67·32	80·71	143·2	99·63	119·5	211·9	1·774	2·127
Carbon disulphide..	20	1·0206	6·36	7·67	13·71	62·30	75·13	134·3	92·21	111·2	198·7	1·787	2·155
Benzene	20	0·9653	5·95	7·14	12·70	61·50	73·98	131·6	91·24	109·5	194·7	1·778	2·134

d-ac-Tetrahydro-2-naphthyl Hydrogen Phthalate.

| Chloroform ... | 22 | 1·0718 | +1·60 | +1·89 | +3·40 | +13·57 | +16·03 | +28·84 | +40·17 | +47·44 | +85·37 | 1·709 | 2·125 |

Brucine Salt of the d-Ester.

| Ethyl alcohol | 22 | 1·0821 | +0·48 | +0·25 | −1·05 | +4·11 | +2·14 | −8·99 | +29·35 | +14·77 | −62·03 | — | — |

l-ac-Tetrahydro-2-naphthyl Hydrogen Phthalate.

Ethyl alcohol	22	0·9830	−1·05	−1·22	−1·85	−9·72	−11·28	−17·11	−28·74	−33·39	−50·64	1·517	1·762
Chloroform ...	22	1·0212	−1·54	−1·04	−3·31	−13·71	−17·27	−29·40	−40·58	−51·12	−87·02	1·706	2·149
Pyridine	22	1·0507	−1·85	−2·33	−3·99	−15·87	−19·00	−34·3	−46·98	−59·17	−101·9	1·712	2·155
Benzene	22	0·4423	−1·34	−1·62	−2·90	−27·54	−33·30	−55·61	−81·53	−98·58	−176·4	1·790	2·164

Cinchonidine Salt of the l-Ester.

| Ethyl alcohol | 22 | 1·1052 | −1·04 | 10·72 | 22·40 | 22·40 | 40·74 | 102·20 | 214·5 | 206·0 | 480·1 | 1·788 | 2·730 |

The solutions for the rotation and most re-mentioned in tables II and III were prepared by making up the amount stated of the respective active ester mcrc made.

TABLE III.

Sodium 1-ac-Tetrahydro-2-naphthyl Phthalate.

Solvent	Length of observation tube, cm.	Weight of solute, grams	α_D	α_{gr}	α_j	$[\alpha]_D$	$[\alpha']_D$	$[\alpha]_j$	$[M]_D$	$[M]_{gr}$	$[M]_j$
Water.........	22	0·5117	±0°	+0·04°	+0·20°	±0°	+0·87°	+5·65°	±0°	+2·77°	+17·96°
„	22	1·0332	±0	+0·07	+0·45	±0	+0·76	+4·84	±0	+2·40	+15·39
„	22	1·5280	−0·17	−0·14	+0·15	−1·24	−1·02	+1·10	−3·93	−3·24	+3·47
„	22	1·0660	−0·45	−0·48	−0·44	−2·54	−2·71	−2·49	−8·09	8·53	−7·82
Ethyl alcohol	22	0·9423	−1·53	−1·83	−2·91	−18·05	−21·69	−34·26	−57·40	−68·66	−108·9

1-a-Tetrahydro-2-naphthyl n-Valerate.

Solvent	Length of observation tube, cm.	Weight of solute, grams	α_D	α_{gr}	α_j	$[\alpha]_D$	$[\alpha']_D$	$[\alpha]_j$	$[M]_D$	$[M]_{gr}$	$[M]_j$
Chloroform	22	0·9867	−4·45	−5·38	−9·48	−41·01	−49·57	−87·34	−95·13	−115·0	−202·6
Ethyl alcohol	20	1·0067	−4·15	−4·98	−8·91	−41·21	−49·45	−88·49	−95·61	−114·8	−205·3
Benzene	20	0·8279	−4·44	−5·35	−9·53	−53·63	−64·63	−115·1	−124·5	−149·9	−267·1
Carbon disulphide.........	20	1·0292	−6·57	−7·96	−14·40	−63·86	−77·36	−140·0	−149·1	−179·5	−324·7

7 and 12) is exhibited the rotations for sodium-yellow light 4·ᴊ
fall on the line so that the ratio violet/yellow is not conꜱᴛᴀ

Experimental.*

ac-*Tetrahydro-2-naphthol.*

The preparation of this compound from β-naphthol by Baꜱꜱᴇꜱ
and Lodter's method (*Ber.*, 1880, **23**, 205) gives only poor ᵧᵢₑ
One cause of this is the loss occasioned when the ethereal ꜱ ᴅᴏ
of the reduced naphthol is washed repeatedly with the ᴀᴢᴏ
solution of sodium diazobenzenesulphonate to remove the ᴄᴏʳ
sponding *ar*-compound. This operation, however, can be ᴀᴠᴏᵢ
and the product converted into hydrogen phthalic esᴛᴇʳꜱ ᴛ
sodium salt of the hydrogen phthalate of *dl-ac*-tetrahydroᵧ ꜱᴀᴏ
crystallises with great readiness from water, and its preᴘᴀʳᴀ
affords a much better method of purifying the *ac*-compoᵤ̨ᵣ ᵧ
the older one.

This *sodium* salt crystallises from water in long needles ᵧ ᴏᵣ
aqueous alcohol in large tablets, has the composition

$$CO_2Na \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{11}, 4H_2O,$$
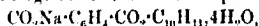
effloresces at about 60°, does not melt below 200°, ᴀᴀᵈ ᵢ ꜱ ᴏ
soluble in ethyl alcohol:

0·3218 lost 0·0582 H_2O and gave 0·0584 Na_2SO_4. H_2O ᵢ ꜱ ᵢ
Na = 5·88.

$C_{18}H_{15}O_4Na, 4H_2O$ requires $H_2O = 18·23$; Na = 5·88 per ᴄᴇ̨ᴛ

The resolution of the *dl*-hydrogen phthalate was carried ᴏ̨ᴛ ᵢ̨
the manner already described (*loc. cit.*), and the results ᴡᴇʳᴇ ᴄ
firmed. The *d*- and *l*-esters form *sodium* salts, which have ꜱᴉ̨ ᵢ
properties to that of the *dl*-ester.

Determinations of Rotatory Power (α¹⁰⁰ min.) *of the Cᴏᴉᵢ̨
l-ac-Tetrahydro-2-naphthyl n-*Valerate in the Homogeneᴏᵤꜱ ꜱ

d-ac-*Tetrahydro-2-naphthol.*

Temp.	28·5°	65°					
αₚ	+80·50°	71·20°	(see also Part III., *loc. cit.*).				
Temp.	27°	59°	82°	126°	136°	156°	1°
αᵧᵣ ...	+96·72°	88·54°	82·00°	71·72	70·58°	66·88	1·2
Temp.	26·5°	58°	84°	126°	137°	157°	1°
α₁₁₁......	+173·60°	158·80°	146·04°	129·64°	126·30°	119·70	1·*

* When not otherwise stated, the experimental procedure is simiᴀᵣ ᵗ ᵗ
previously described (*loc. cit.*).

lac-*Tetrahydro-2-naphthyl* n-*Valerate.*[*]

	20°	44°	54°	110°	135	161°
	$-48\cdot12°$	$46\cdot24°$	$45\cdot64°$	$40\cdot16°$	$38\cdot36$	$35\cdot80$
	20°	43°	59°	110°	138°	160°
	$-37\cdot80°$	$55\cdot86°$	$54\cdot44°$	$50\cdot22°$	$47\cdot84$	$46\cdot00°$
	20°	41°	59°	110°	136°	162°
	$-102\cdot78°$	$-99\cdot90°$	$-96\cdot52°$	$-89\cdot60°$	$85\cdot00$	$84\cdot20°$

CLI.—*The Reduction Products of Ethyl Hydrindene-*
2 : 2-dicarboxylate.

By JAMES KENNER.

In a previous communication it was suggested that the ease with which cyclic condensation occurs should be modified by the presence within it of certain carbon atoms which, being already members of a closed ring, have the directions of their valencies to some extent determined (Kenner and Turner, T., 1911, **99**, 2102). The investigation now to be described was undertaken with the object of studying ring-formation from compounds, the molecules of which contain one carbon atom fulfilling this condition; in other words, the preparation of *spiro*-compounds was to be attempted.

As substituent groups are also known to be important factors in determining the facility of formation, and stability, of cyclic compounds it appeared that, among *spiro* compounds, the hydro-acids would furnish the most decisive evidence of the influences referred to in the preceding paragraph. These and other considerations suggested the application to ethyl hydrindene 2 : 2 dicarboxylate of Bouveault and Blanc's method of reduction by means of

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[*] These rotations are somewhat lower than those previously published. It has been thought necessary to investigate the cause of the discrepancy, as this paper deals with optical dispersive power, which is only very slightly affected by this discrepancy.

sodium and ethyl alcohol, in the hope of preparing *αα'-dimethyl*
2:2-*dimethylhydrindene* (I), from which the hydrocarbon

$$C_6H_4\!\!<^{CH_2}_{CH_2}\!\!>\!\!C\!\!<^{CO_2Et}_{CO_2Et} \rightarrow C_6H_4\!\!<^{CH_2}_{CH_2}\!\!>\!\!C\!\!<^{CH_2 \cdot OH}_{CH_2 \cdot OH} \rightarrow$$
$$\text{(I.)}$$

$$C_6H_4\!\!<^{CH_2}_{CH_2}\!\!>\!\!C\!\!<$$
$$\text{(II.)}$$
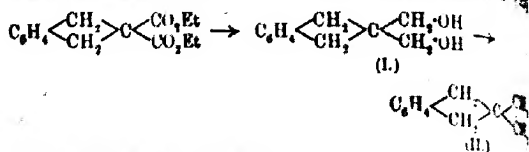
might subsequently be obtained.

It had previously been shown by Bouveault and Blanc that *ethyl*
di*iso*butylmalonate, whilst furnishing a certain amount of the
expected glycol, was to a considerable extent decomposed in the
following way under the influence of sodium ethoxide formed
during the reaction :

$$(C_4H_9)_2C(CO_2Et)_2 + C_2H_5 \cdot OH \rightarrow (C_4H_9)_2CH \cdot CO_2Et + CO_2Et,$$

the ethyl *iso*valerate being then reduced in the normal manner
(*Bull. Soc. chim.*, 1904, [iii], **31**, 1203).   Ethyl hydrindene-
oxylate had, however, been shown by Thole and Thorpe to be
quite stable towards sodium ethoxide at the ordinary temperature
(T., 1911, **99**, 2186), and the hope was therefore entertained that
even at the higher temperature to be used in these experiments the
type of decomposition observed by Bouveault and Blanc might not
assert itself in a marked degree.   This expectation, however, was
not realised, for the yield of the glycol (I) was disappointingly
small, being less than 3 per cent. of the calculated.   More than
40 per cent. of the ethyl hydrindenedicarboxylate was converted
into 2-*hydroxymethylhydrindene* (III), the remainder being re-
covered in the form of a mixture of hydrindene-mono- and -di-carb-
oxylic acids, in which the former largely predominated.

$$C_6H_4\!\!<^{CH_2}_{CH_2}\!\!>\!\!CH \cdot CH_2 \cdot OH.$$
$$\text{(III.)}$$
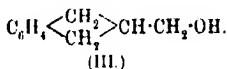
Initially, therefore, the dicarboxylic ester was almost entirely
converted into the monocarboxylic ester, and, in the author's
opinion, this reaction must be ascribed to spatial causes to
will be discussed later.   It is probable that such influences also play
a part, although possibly a subordinate one, in promoting the
decompositions discussed by Thole and Thorpe (*loc. cit.*).

2-Hydroxymethylhydrindene was readily converted by the usual
means into 2-*bromomethylhydrindene* (IV), the reaction of which

$$C_6H_4\!\!<^{CH_2}_{CH_2}\!\!>\!\!CH \cdot CH_2Br \qquad\qquad CH_3 \cdot CH\!\!<^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}\!\!>\!CH \cdot R.$$
$$\text{(IV.)} \qquad\qquad\qquad\qquad \text{(V.)}$$
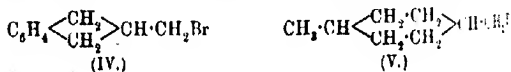
ried investigation, because it has frequently been observed that
, bromine atom in derivatives of this type is remarkably inert.
us Perkin and Pope found that 1-methyl-4-bromomethyl*cyclo*-
xane (V) was converted into the cyanide only with considerable
fruity (T., 1908, **93**, 1079). Similar relationships were dis-
rered in the present instance. The bromo-compound was un-
anged after prolonged boiling with amalgamated zinc and hydro-
loric acid, in spite of the efficiency of this reducing agent (Clem-
msen, *Ber.*, 1913, **46**, 1837; 1914, **47**, 51, 681). Interaction of
, bromo-compound and ethyl sodiomalonate in alcoholic solution
lor ten hours at the boiling point resulted in the production of
b about 65 per cent. of the calculated amount of *ethyl 2-hydrin-*
methylmalonate (VI):

$$H_4\underset{C H_2}{\overset{C H_2}{<}}>CH \cdot CH_2 Br + CHNa(CO_2Et)_2 \longrightarrow$$

$$C_6H_4\underset{C H_2}{\overset{C H_2}{<}}>CH \cdot CH_2 \cdot CH(CO_2Et)_2$$
$$(VI.)$$
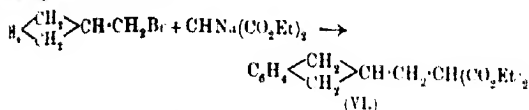
The formation of 2-*phthaliminomethylhydrindene* (VII) by heat-
, the bromo-derivative with potassium phthalimide at 180—200°
r nine hours was similarly incomplete:

$$H_4\underset{C H_2}{\overset{C H_2}{<}}>CH \cdot CH_2 Br + C_6H_4\underset{CO}{\overset{CO}{<}}>NK \longrightarrow$$

$$C_6H_4\underset{C H_2}{\overset{C H_2}{<}}>CH \cdot CH_2 \cdot N\underset{CO}{\overset{CO}{<}}>C_6H_4$$
$$(VII.)$$
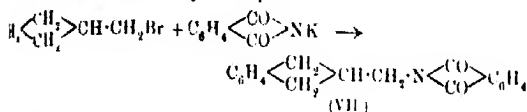
The contrast between the inertia of the bromine atom in such
spounds and its activity in, for instance, benzyl bromide, is
rthy of some comment, and is obviously in some way connected
it the difference between the saturated and the unsaturated
ditions of the cyclic structures present in the two types of
:pounds. If, however, benzyl bromide be represented by the
mula (VIII), in Flürscheim's notation, it would appear to follow
a striking consequence that Perkin and Pope's 1-methyl-4-bromo-
methyl*cyclo*hexane is to be represented by the formula IX:

$$\overset{}{\underset{(VIII.)}{\diagdown} —CH_2—Br}$$

$$CH_3 \cdot CH\underset{CH_2 \cdot CH_2}{\overset{CH_2 \cdot CH_2}{<}}>CH—CH_2—Br$$
$$(IX).$$
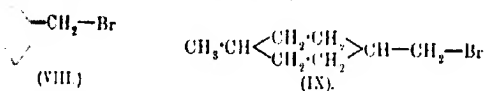
The similar inertia of the bromine atoms in tetrabromotetra-
methylmethane (Perkin and Simonsen, T., 1905, **87**, 161; Fecht,
*., 1907, **40**, 3884) would then find expression in the formula X:

$$\overset{Br—CH_2}{\underset{Br—CH_2}{>}}C\underset{CH_2—Br}{\overset{CH_2—Br}{<}}$$
$$(X.)$$
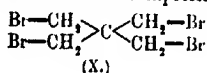
The facts symbolised by these formulæ are illustrative of the influences referred to at the commencement of this paper, and, in the author's opinion, they are all explicable by a thorough application of Baeyer's strain theory. For it is at once clear that the normal relative positions of substituents known to exert steric hindrance, such as methyl (or bromomethyl) and carboxyl groups may, when they are attached to the same carbon atom, be comparable, in regard to this atom, with those of the carbon atoms of, for instance, a cyclohexane or a cycloheptane ring. Then, applying Werner's conception of the uniform spherical distribution of affinity round a carbon atom (" Beiträge zur Theorie der Affinität und Valenz," Zurich, 1891), we see that, if aa' in XI represents a section the zones of affinity appropriated by two univalent groupings in the plane of the paper when "the angle between two valencies is 109°28'," an increase in this angle will cause an alteration in the relative position of the zones, which will now be represented by XII:
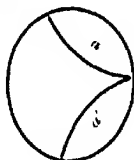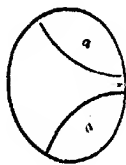
(XI.)   (XII.)

In this manner a certain amount of affinity, corresponding to the region (b), will be left unsatisfied, and the extent of this region is a measure of the "strain," in Baeyer's terminology. If the groups attached to the carbon atoms be free to move, they will probably so adjust themselves as partly to engage the valency left free because the change in position of the zones aa' means an incursion into the zones of affinity previously available for them.

In the following paragraphs, the attempt is made to apply these considerations to the cases in which (a) two of the groups attached to a carbon atom are components of the same cyclic system, whilst the other two are groups of large molecular volume. In this case the motion of the former groups is restricted, and the affinity represented by b will then remain free and available to a greater or less extent as partial valency to an atom situated above or below the plane of the paper and, for example, coplanar with the groups appropriating aa'.

Thus, in the case of ethyl hydrindenedicarboxylate there will be residual affinity on the quaternary carbon atom, and, owing to the encroachment of the carbethoxy-groups on the zones of affinity

ually available for the two carbon atoms of the hydrindene ring,
er more of these groups will obtain less than its proper share
finity. This deduction is in agreement with the experimental
ence just advanced, according to which we may conclude that
ester is more adequately represented by the formula XIII:

$$C_6H_4\left\langle{CH_2 \atop CH_2}\right\rangle C\left\langle{CO_2Et \atop CO_2Et}\right.$$
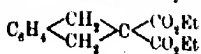
(XIV.)

similar considerations probably supply an explanation of a
ber of reactions met with in the chemistry of cyclic compounds.
illustration of this may be cited the change of carone into
ketone by distillation (Baeyer, *Ber.*, 1894, **27**, 1917), and into
one and hydroxy-menthanone by absorption of the elements
hydrogen bromide or water (*ibid.*, p 1920); the isomerisation
carylamine hydrochloride into vestrylamine hydrochloride
ayer, Ber., 1894, **27**, 3486); the disruption of the bridge
dimethyldicyclopentanonecarboxylic acid by reduction (Perkin,
ye. and Walker, **T.**, 1901, **79**, 729); the addition of the
ents of hydrogen bromide to α-camphylic acid (Perkin, T.,
83, 842); and the various reactions by which the bridge in
camphor molecule is broken between two quaternary carbon
see Aschan, "Konstitution des Kamphers," Braunschweig,
3, p. 79).

se reactions of certain other compounds are illustrative of
ther mode of relieving the stress on the quaternary carbon atom,
ely, the replacement of two single bonds by a double bond.
results in a smaller demand being made on the affinity of the
tral carbon atom. Thus Wallach has shown that ethyl *cyclo*-
 x-1-ol-1-acetate on hydrolysis is partly converted into *cyclo*-
tone, accompanied by some *cyclo*hexanol (a hydrogen atom
displaced a group of large molecular volume). Further,
dration of the ester or of the acid is easily carried out, and
ts in the formation of Δ¹-*cyclo*hexeneacetic acid or of carboxy-
lene*cyclo*hexane, according to the agent employed. Indeed,
initial condensation product of 1:5-dimethyl-Δ¹-*cyclo*hexen-3-
cannot be isolated, but passes over at once into 1:5-dimethyl-
*cyclo*hexadienyl-3-acetic acid (*Annalen*, 1900, **314**, 147; 1902,
325; 1905, **343**, 40, **347**, 316; 1908, **360**, 26). That these
ions are not due to the presence of the hydroxyl group as
is shown by a remarkable instance of an analogous kind, com-
nicated to the author by Prof. J. F. Thorpe. Ethyl *cyclo*-
ane-αα'-dibromodiacetate (XIV) when boiled with dilute potass-
hydroxide solution is converted into carboxymethylene*cyclo*-

hexane (XV), although when it is dropped into concentrated aqueous potassium hydroxide at 130° the acid (XVI) is produced

$$CH_2\underset{CH_2 \cdot CH_2}{\overset{CH_2 \cdot CH_2}{<}}>C\underset{CHBr \cdot CO_2Et}{\overset{CHBr \cdot CO_2Et}{<}} \longrightarrow$$
(XIV.)
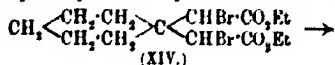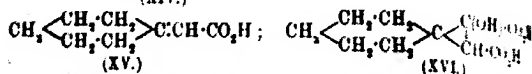
$$CH_2\underset{CH_2 \cdot CH_2}{\overset{CH_2 \cdot CH_2}{<}}>C{:}CH \cdot CO_2H \; ; \quad CH_2\underset{CH_2 \cdot CH_2}{\overset{CH_2 \cdot CH_2}{<}}>C\underset{CH \cdot CO_2H}{\overset{C(OH) \cdot O_2H}{<}}$$
(XV.)   (XVI.)

It is obvious that similar conditions will prevail when, as in the instances quoted above, three or four separate groups of large molecular volume are attached to a single carbon atom.

When, as in the molecule of *cyclo*propane-1 : 1-dicarboxylic acid the cyclic structure is such that the "angle between two valencies of the quaternary carbon atom is less than 109°28′, the effect just discussed will be intensified. Hence this acid and 1 : 1-methyl*cyclo*propane are almost comparable with unsaturated compounds in the readiness with which they take part in additive reactions, and the general conclusions of Kötz (*J. pr. Chem.*, 1903, [ii], **68**, 174) in regard to the derivatives of *cyclo*propane are in agreement with the statement just made. Further, Radulescu's observation that the acid (XVII) is stable toward halogen hydrides (*Ber.*, 1909, **42**, 2771; 1911, **44**, ...) appears to be direct evidence in favour of the suggestion that the carbonyl groups are differently situated with regard to the central carbon atom from those in *cyclo*propane-1 : 1-dicarboxylic acid
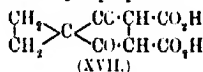
$$\underset{CH_2}{\overset{CH_2}{>}}C\underset{CO \cdot CH \cdot CO_2H}{\overset{CO \cdot CH \cdot CO_2H}{<}}$$
(XVII.)

The rearrangement of derivatives of ethylene oxide into those of acetaldehyde are instances of a similar nature among heterocyclic compounds (Fourneau and Tiffeneau, *Compt. rend.*, 1905, **141**, 662; Klages, *Ber.*, 1905, **38**, 1969; Klages and Kessler, *Ber.*, 1906, **39**, 1753):

$$\underset{CH_2}{\overset{CPh_2}{>}}O \; \longrightarrow \; \underset{CHO}{\overset{CHPh_2}{\quad}} \; ; \quad \underset{CH_2}{\overset{CPhMe}{>}}O \; \longrightarrow \; \underset{CHO}{\overset{CHPhMe}{\quad}}$$
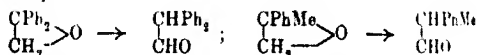
Both pairs of valencies attached to the carbon atom (?) are inclined to one another at angles less than 109°28′, when some instability of the molecule may be expected. Thus the following table shows in the case of the central carbon atom of the type compound, $(CH_2)_xC(CH_2)_y$, the angle between a valency of a $(x + 1)$-membered ring and one of the $(y + 1)$-membered ring.

$x + 1$	$y+1$		
	2	3	4
2	180	150′	135°
3		139	128

magnitude of these angles indicates that considerable
amts of unsatisfied affinity will exist between the zones corre-
ding with the valencies in question. Consequently, compounds
ns type may be very difficult to isolate, and, when obtained,
liable to undergo change. Thus Dimroth and Feuchter were
le to prepare an allene derivative from the compounds XVIII
XIX (*Ber.*, 1903, **36**, 2238; compare Ipatiev, *J. pr. Chem.,*
, [ii], **59**, 517):

$$\underset{CO_2Et}{\overset{C_6H_5}{>}}C:CCl\cdot CH_2\cdot CH_2 \qquad \underset{CO_2Et}{\overset{C_6H_5}{>}}CH\cdot CC:CH\cdot CH_3$$

$$(XVIII.) \qquad\qquad\qquad (XIX.)$$
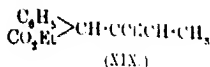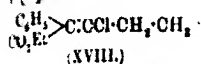
larly, ethyl allenetetracarboxylate (XX), which is only
ned by heating the initial product (XXI) of the action of
sodiomalonate on carbon tetrachloride, absorbs two molecular
ortions of water when exposed in a moist atmosphere (Zelinski
Doroschevski, *Ber.*, 1894, **27**, 3376):

$$+ 2Na_2C(CO_2Et)_2 + C_2H_5\cdot OH \rightarrow CH\underset{C(OEt)(CO_2Et)_2}{\overset{C(CO_2Et)_2}{<}} \rightarrow$$

$$(XXI.)$$

$$C\underset{C(CO_2Et)_2}{\overset{C(CO_2Et)_2}{\lessgtr}}$$

$$(XX.)$$
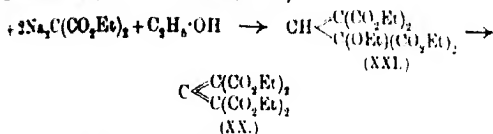
e action of alcoholic potassium hydroxide on iodomethyl*cyclo*-
ane leads to the production of erythrene, presumably owing to
earrangement of methylene*cyclo*propane (Demjanov, *J. Russ.*
. Chem. Soc., 1903, **35**, 375):

$$\underset{CH_2}{\overset{CH_2}{>}}CH\cdot CH_2I \rightarrow \left[\underset{CH_2}{\overset{CH_2}{>}}C:H_2\right] \rightarrow \underset{CH_2}{\overset{CH}{\diagdown}}CH:CH_2.$$
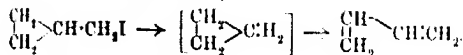
o, Favorski and Batalin have recently shown (*Ber.*, 1914,
1648) that Gustavson was mistaken in attributing the consti-
a of an ethylidene*cyclo*propane to a compound he had prepared
analogous manner (*Compt. rend.*, 1896, **123**, 242). Further,
ole product of dehydration of *cyclo*propyldimethylcarbinol is
β-propyl*iso*propylene (XXII), notwithstanding the fact that

$$OH\cdot C(CH_3)_2\cdot CH\underset{CH_2}{\overset{CH_2}{<}} \rightarrow CH_2:C(CH_3)\cdot CH\underset{CH_2}{\overset{CH_2}{<}}$$
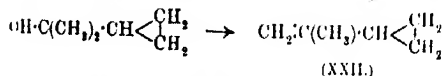
$$(XXII.)$$

hyl*iso*propylcarbinol furnished the isomeric olefines (XXIII
XXIV) in the proportion of three to one (Henry, *Compt. rend.*,
147, 557):

$$C(CH_3)_2\cdot CH(CH_3)_2 \rightarrow C(CH_3)_2:C(CH_3)_2 \text{ and }$$

$$(XXIII.)$$

$$CH_2:C(CH_3)\cdot CH(CH_3)_2.$$

$$(XXIV.)$$
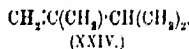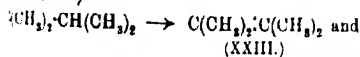
The production of methylene*cyclo*butane (XXV), in of spiro
*spiro*pentane (XXVI), from tetrabromotetramethylmethane
doubtless to be ascribed to similar causes (Demjanov, *Ber.*
41, 915; Favorski and Batalin, *loc. cit.*; compare Gskin
and Bulatov, *J. pr. Chem.*, 1896, [ii], **54**, 97; **56**, 93, *Ber.*
loc. cit.; Zelinski, *Ber.*, 1913, **46**, 170):

$$\begin{array}{c}\text{CH}_2\text{Br}\\ \text{CH}_2\text{Br}\end{array}\!\!>\!\text{C}\!<\!\begin{array}{c}\text{CH}_2\text{Br}\\ \text{CH}_2\text{Br}\end{array} \longrightarrow \begin{array}{c}\text{CH}_2\text{·C:CH}_2\\ \text{CH}_2\text{·CH}_2\end{array}; \quad \begin{array}{c}\text{CH}_2\\ \text{CH}_2\end{array}\!\!>\!\text{C}\!<\!\begin{array}{c}\text{CH}_2\\ \text{CH}_2\end{array}$$
$$\qquad\qquad\qquad (\text{XXV.}) \qquad\qquad (\text{XXVI.})$$
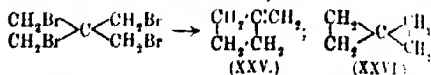
Neither this hydrocarbon nor *cyclo*butanone (Kishner, *J. Russ.
Phys. Chem. Soc., 1905, **37**, 106; 1907, **39**, 922) exhibits a
tendency towards the breaking down of the four-membered ring,
but it is significant that *cyclo*butane-1 : 3-dione behaves as though
it were represented by the formula XXVII (Chick and Wilson,
T., 1910, **97**, 1982):

$$\begin{array}{c}\text{CH}_2\text{·C}\!\!<\!\!^0\\ |\\ \text{O:C·CH}_2\text{---}\end{array}$$
$$(\text{XXVII.})$$
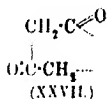
The illustrations thus brought forward are not intended to
exhaustive, but suffice to indicate the aspect from which, in the
author's opinion, the study of *spiro*-compounds should be
approached. The quaternary carbon atom is not *per se* a point
of weakness, this being conditioned by the distortion of its valencies
from their normal positions.

Finally, it may be mentioned that experiments have also been
initiated with a view, on the one hand, to the synthesis of
compound (XXVIII) by the condensation of the chloride of *hydrin*-
dene-2 : 2-dicarboxylic acid with benzene, and, on the other, to

$$\text{C}_6\text{H}_4\!\!<\!\!\begin{array}{c}\text{CH}_2\\ \text{CH}_2\end{array}\!\!>\!\text{C}\!<\!\begin{array}{c}\text{COCl}\\ \text{COCl}\end{array} + \text{C}_6\text{H}_6 \longrightarrow \text{C}_6\text{H}_4\!\!<\!\!\begin{array}{c}\text{CH}_2\\ \text{CH}_2\end{array}\!\!>\!\text{C}\!<\!\begin{array}{c}\text{CO}\\ \text{CO}\end{array}\!\!>\!\text{C}_6$$
$$\qquad\qquad\qquad\qquad (\text{XXVIII.})$$
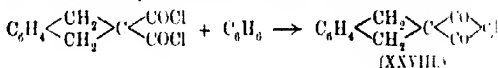
preparation of reduction products of ethyl *cyclo*hexane diesters
from which *spiro*-compounds might be prepared. The investigation
in this direction has, however, only just been commenced, and the
measure of success attained is indicated in the experimental part
of this paper.

EXPERIMENTAL.

Reduction of Ethyl Hydrindene-2 : 2-dicarboxylate

Sodium (30 grams), cut into pieces the size of a pea, was placed
in a large flask, fitted with a long, upright condenser and a
funnel, and the flask was heated to 80° in an oil-bath. A solution

...late alcohol of ethyl hydrindenedicarboxylate (23 grams), ...ly purified by distillation under diminished pressure ...c.), was then run from the tap-funnel on to the sodium as ...ly as possible, consistent with efficient action of the condenser. ...temperature of the oil-bath was then raised to 130°, and a ...er quantity of alcohol (100 c.c.) gradually added in the course ...so hours. At the end of five hours from the experiment any ...duced ester was hydrolysed by the gradual addition of water ...e mixture. The product was then cooled, considerably diluted, ...treated with sufficient sulphuric acid to leave the solution ...ly alkaline. By exhaustive extraction with ether the mixture ...duction products was removed, whilst hydrindenemonocarb-...acid (5 5 grams) could be recovered by subsequent acidifica-...of the aqueous solution.

...ethereal extracts, after treatment in the usual manner, ...ed an oil, which was distilled under diminished pressure. ...s manner a large fraction (5·5 grams) was obtained, which ...at about 140°/11 mm. and solidified at the ordinary tem-...ure.

...*ydroxymethylhydrindene* (III), obtained in this way, has a ...cteristic agreeable odour, and consists of prismatic crystals, ...melt at 33° and boil at 139—140°/11 mm. It is readily ...in most organic solvents, but only sparingly so in light ...eum (b. p. 40—50°), and may be crystallised from this
...

...gave 0·4424 CO$_2$ and 0·1078 H$_2$O. C = 80·98; H 8·04.
    C$_{13}$H$_{12}$O requires C = 81·07; H = 8·11 per cent.

...*phenylurethane*, C$_6$H$_4$<$^{CH_2}_{CH_2}$>CH·CH$_2$·O·CO·NH·C$_6$H$_5$, was
...ed by heating a solution of molecular proportions of the
...ol and phenylcarbimide in light petroleum (b. p. 90—110°).
...crystallisation, it melted at 99·5°:

...gave 10·2 c.c. N$_2$ at 11° and 755 mm. N 5·59.
    C$_{17}$H$_{17}$O$_2$N requires N = 5·24 per cent.

...*ydroxy-2:2-dimethylhydrindene* (I) was obtained by dis-...the united residues from four of the above preparations of ...oxymethylhydrindene. A colourless oil passed over at about ...mm., and rapidly solidified. On the addition of light ...eum (b. p. 90—110°) to its solution in ethyl alcohol, small, ...nal prisms, melting at 112·5°, separated. The yield was ...s:

...gave 0·4266 CO$_2$ and 0·1090 H$_2$O. C = 74·20; H = 7·73.
    C$_{11}$H$_{14}$O$_2$ requires C = 74·16; H = 7·86 per cent.

Reduction of Ethyl Hydrindene-2-carboxyl...

A solution of the ester (20 grams) in alcohol (100 c c) was added to sodium (18 grams) in precisely the same manner as described for the previous case, alcohol (20 c.c.) being subsequently added. The yield of carbinol was 8·5 grams.

2-Aldehydohydrindene, $C_6H_4{<}^{CH_2}_{CH_2}{>}CH \cdot CHO$.
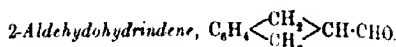
2-Hydroxymethylhydrindene (10 grams), having been added a solution of chromic acid (4·2 grams) in 10 per cent. sulphuric acid (75 grams), the mixture was heated on the water bath for two hours. The ethereal extract of the cooled solution was washed with sodium carbonate solution, and then shaken with excess of sodium hydrogen sulphite solution. The aldehyde, isolated in poor yield from this solution in the usual manner by decomposing with sodium hydrogen carbonate, was a fairly mobile oil, boiling at 122°/12 mm., which did not solidify. It readily underwent oxidation on exposure, and its odour also characterised it as an aliphatic aldehyde:

0·1440 gave 0·4325 CO_2 and 0·0878 H_2O. C=81·91; H=6·77.
$C_{10}H_{10}O$ requires C=82·19; H=6·85 per cent.

The semicarbazone, prepared in the usual manner, to this dissolved in alcohol, and separated from this solvent in minute clusters of small needles melting at 174°:

0·1120 gave 20·6 c.c. N_2 at 17° and 730 mm. N=20·96.
$C_{11}H_{13}ON_3$ requires N=20·69 per cent.

2-Bromomethylhydrindene (IV).

This compound was easily prepared by heating a solution of 2-hydroxymethylhydrindene (35 grams) in glacial acetic acid saturated at 0° with hydrogen bromide (50 c.c.), at 100—110° for three and a-half hours.

The compound boiled at 132°/11 mm., and solidified at low temperatures to masses of magnificent prisms, melting at ·. Its odour was characteristic and reminiscent of aniseed:

0·1742 gave 0·3646 CO_2 and 0·0812 H_2O. C=57·08; H=5·22.
$C_{10}H_{11}Br$ requires C=56·87; H=5·21 per cent.

It was recovered unchanged after being boiled for ten hours with amalgamated zinc and dilute hydrochloric acid.

Interaction of 2-Bromomethylhydrindene with Ethyl Malonate.

Ethyl malonate (6·4 grams) and the bromo-compound (8·4 grams) were successively added to a solution of sodium (0·9 gram) in alcohol (cc.). At the temperature of the water-bath a separation of sodium bromide soon commenced, and after ten hours the product worked up in the usual manner. By distillation under reduced pressure, well-defined fractions of ethyl malonate, bromomethylhydrindene, and finally of the desired ester (7·5 grams) obtained.

Ethyl 2-hydrindylmethylmalonate (VI) is a colourless liquid, it boils at 211°/15 mm., and does not solidify even when cooled freezing mixture:

·394 gave 0·4092 CO_2 and 0·1074 H_2O. C 70·00; H 7·48

$C_{17}H_{22}O_4$ requires C = 70·35; H = 7·59 per cent.

The corresponding *acid* was prepared by hydrolysis with alcoholic sodium hydroxide, and separated from its solution in alcohol in crystals of small, transparent plates, melting at 174°:

·146 gave 0·4285 CO_2 and 0·0965 H_2O. C 66·93; H 6·14.

$C_{13}H_{14}O_4$ requires C = 66·66; H = 6·00 per cent.

The *barium, calcium, lead, tin,* and *ferric* salts are insoluble in water, whilst its *magnesium, copper,* and *cobalt* salts are soluble in water.

The *dihydrazide,* $C_6H_4\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}CH \cdot CH_2 \cdot CH(CO \cdot NH \cdot NH_2)_2$, crys-

from alcoholic solution in silky needles melting at 177°:

·35 gave 35·6 c.c. N_2 at 23° and 747 mm. N 21·6.

$C_{13}H_{18}O_2N_4$ requires N = 21·4 per cent.

Hydrindylpropionic acid, $C_6H_4\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$,

prepared by heating the above acid at 190° until the evolution of carbon dioxide had ceased. It was readily soluble in benzene, sparingly so in hot light petroleum (b. p. 90—110°), and crystallised from a mixture of these solvents in small plates melting 96°:

·35 gave 0·4902 CO_2 and 0·1166 H_2O. C 76·05; H 7·37.

·174 required 14·6 c.c. N/10-NaOH. Equivalent 189·7.

$C_{12}H_{14}O_2$ requires C = 75·79; H = 7·37 per cent. M.W. 190.

The *barium* and *magnesium* salts are soluble in cold water, whilst calcium salt is sparingly soluble, and separates from its solution in water in needles. Its *ferric, copper,* and *cobalt* salts are soluble in hot water, its *lead* and *tin* salts sparingly so, and its iron salt turns yellow when boiled with water.

2-Phthaliminomethylhydrindene (VII).

An intimate mixture of 2-bromomethylhydrindene (12 grams) with potassium phthalimide (9 grams) was heated at 180° for nine hours in an apparatus provided with a reflux tube. The mixture solidified on cooling, and required to be finely powdered before adherent oily matter could be removed by repeated extraction with hot light petroleum (b. p. 90—110°). Potassium bromide having then been removed by extraction with hot water, the residue was crystallised from glacial acetic acid. The compound separated in small, slender prisms, which were usually somewhat discoloured, and melted at 174°. The yield was 57 per cent. of the theoretical, and was not improved by carrying out the condensation in presence of sodium iodide:

0·1984 gave 9·0 c.c. N_2 at 16° and 752 mm.   N = 5·36.

$C_{18}H_{15}O_2N$ requires N = 5·05 per cent.

2-Hydrindylmethylamine, $C_6H_4 <^{CH_2}_{CH_2}> CH \cdot CH_2 \cdot NH_2$.
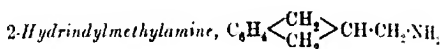
Phthaliminomethylhydrindene (8 grams) was heated with concentrated hydrochloric acid (35 c.c.) at 180—200° for six hours, and the product was then treated in the usual manner. A small proportion of the phthalimino-derivative remained unchanged, but four such experiments furnished a sufficient quantity of the base, boiling at 248°, to permit of its characterisation.

The *hydrochloride* separated from its solution in dilute hydrochloric acid in thin plates with a satiny lustre, melting and decomposing at 258—260°:

0·1890 gave 12·4 c.c. N_2 at 15° and 751 mm.   N = 7·63.

$C_{10}H_{13}N,HCl$ requires N = 7·63 per cent.

The *platinichloride* was obtained as a yellow powder, decomposed at 233°:

0·3614 gave 0·1008 Pt.   Pt = 27·89.

$(C_{10}H_{13}N)_2,H_2PtCl_6$ requires Pt = 27·70 per cent.

The *iodide, sulphate, oxalate,* and *phosphate* are readily soluble in water, whilst the *carbonate* (prismatic needles) and *dichromate* (orange, prismatic needles) are soluble in hot water.

2-Phenylthiocarbamidomethylhydrindene,

$$C_6H_4 <^{CH_2}_{CH_2}> CH \cdot CH_2 \cdot NH \cdot CS \cdot NH \cdot C_6H_5,$$
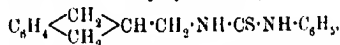
crystallises from alcohol in hexagonal plates melting at 145°.

0·1760 gave 15·5 c.c. N_2 at 16° and 745 mm.   N = 10·26.

$C_{17}H_{18}N_2S$ requires N = 9·93 per cent.

The Chloride of Hydrindene-2:2-dicarboxylic Acid,

$$C_6H_4{<}{}^{CH_2}_{CH_2}{>}C(COCl)_2.$$
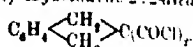
This compound was prepared by the interaction of the calculated weights of hydrindenedicarboxylic acid and phosphorus penta-chloride. It boiled at 173—175°/20 mm., and solidified at the ordinary temperature. It crystallised from light petroleum (b. p. 40°) in clusters of rectangular plates, which melted at 45°, and did not exhibit any marked tendency towards decomposition on contact with the atmosphere:

0.1516 gave 0.2952 AgCl. Cl = 29.02.

$C_{11}H_8O_2Cl_2$ requires Cl = 29.22 per cent.

An attempt was made to condense this compound with benzene under the conditions employed by Freund (*Annalen*, 1910, **373**, 1) in the case of diethylmalonyl chloride. It was found that, as in the latter case, the liquor obtained by steam distillation of the product was coloured green, and a small quantity of golden yellow oil was obtained by extraction with ether. There can, there-fore, be no doubt that the reaction took the desired course.

Reduction of Ethyl cycloHexanediacetate.

This operation was carried out in the manner already described in the case of ethyl hydrindenedicarboxylate. The oil obtained boiled indefinitely, but small quantities of solid matter separated in the later fractions, boiling at 195—200°/21 mm. This product was sparingly soluble in light petroleum (b. p. 60—80°), and moderately so in benzene. By crystallisation from this solvent needles, melting at 123°, were obtained :

0.1406 gave 0.2848 CO_2 and 0.1046 H_2O. C = 70.23; H = 10.51.

$C_6H_{14}O_2$ requires C = 70.06; H = 10.06 per cent.

The author hopes to prosecute his investigations in the direction indicated as soon as circumstances permit a resumption of the experiments.

THE UNIVERSITY,
SHEFFIELD.

CCLII.—*Studies in the Succinic Acid Series. Part II.
Anilides and Anilic Acids, and the Influ...
Steric Hindrance on the Formation of the Anil...*

By George Francis Morrell.

The method of Bouveault and Blanc (*Bull. Soc. chim.*
[iii], **33**, 879) for the conversion of acids into the corresponding
alcohols by reduction of their esters in alcoholic solution by
sodium frequently gives very unsatisfactory results with the
basic acids of the aliphatic series (compare Harries, *Annalen*
383, 167). The original intention of studying the reduction
other open-chain derivatives of dibasic acids was hindered by a
lack of suitable methods for preparing them in quantity. This
especially the case with the derivatives of the succinic acid, when
ring-formation takes place so readily, and the open-chain deriv-
ative forms either a small fraction of the product, or is entirely
absent.

The present communication deals with an investigation
methods and conditions requisite for the production of a good
yield of certain of the open-chain aniline and ammonia deriv-
of succinic acid and its homologues. Whilst with several
succinic acids the neutral anilides were, under all conditions,
duced only in traces by the action of aniline on the acids and
anil was generally the sole product, in the case of succinic a
the aniline could, by repeated treatment of the succinamic acid,
as a by-product, be prepared in excellent yield by the met
under specified conditions. The formation of the five-membe
ring is, therefore, apparently facilitated by the presence of met
substituents in the succinic acid. Where the "direct met
of preparation failed, good results were obtained by the ac
of aniline on the acid chlorides.

The anilic acids are of importance on account of their use
the characterisation of the dibasic acid by Auwers' method
the investigation has here been limited to methylsuccinanilic ac
as the others have already been fully described by other writ
From an unsymmetrically substituted succinic acid, two isom
anilic acids can theoretically be derived, but although met
succinanilic acid has been prepared in different ways by
investigators, only one of these possible isomerides has ever be
isolated. Arppe and Biffi (*Annalen*, 1854, **90**, 111; 91, 3
obtained an anilic acid, melting at 147°, from the anil by open
the ring with alkali. Anschütz (*Annalen*. 1888, **246**, 12... 34

B. likewise prepared the anilic acid both by Arppe's method and by two methods of his own, namely, the reduction of mesaconilic acid, and the action of aniline on methylsuccinic anhydride. In all cases the acid obtained melted at 143°. Later, Bone and Sprankling (T., 1899, **75**, 860) give 148–149° as the melting point, and specifically state that they were unable to isolate any isomeric acid. Auwers (*Annalen*, 1896, **292**, 195) ascribes the formation of only one anilic acid to the influence of the unsymmetric molecule, which thus determines the sense in which the aniline is added to the anhydride, or sodium hydroxide to the anil. Thus, for example, reaction (1) might proceed to the entire exclusion of reaction (2):

(1) $CH_3 \cdot CH-CO$
$\quad CH_2 \cdot CO$ $\rightarrow$ $CH_3 \cdot CH \cdot CO_2H$
$\qquad\qquad\qquad\qquad CH_2 \cdot CO \cdot NH \cdot C_6H_5$

(2) $CH_3 \cdot CH-CO$
$\quad CH_2 \cdot CO$ $\rightarrow$ $CH_3 \cdot CH \cdot CO \cdot NH \cdot C_6H_5$
$\qquad\qquad\qquad\qquad CH_2 \cdot CO_2H$
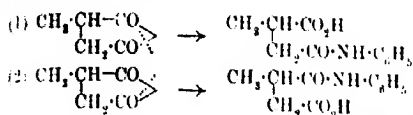
In support of this idea, he states that in the case of methylsuccinic acid, where the lack of symmetry is not so pronounced, two isomeric anilic acids were isolated.

In preparing methylsuccinanilic acid, whether from the anil, from the anhydride, two points of interest were noted which seem to indicate the incorrectness of Auwers' and Bone's assumption and the existence of two isomerides in the product. It was noted that the anilic acid was always precipitated as an oil, which solidified slowly on keeping, and that never more than about 10 per cent. of the theoretical yield of the acid, melting 143°, could be isolated. Both of these observations were quite at variance with those made in the otherwise perfectly analogous case of succinanilic acid. It seemed scarcely possible that the presence of an isomeric acid could have been overlooked by so many investigators, and, indeed, the evaporation of the aqueous mother liquors to dryness yielded only a very soluble, viscid residue, which, however, was sufficient in amount to account for the deficient yield. It was not until it was discovered that both acids in question were, in aqueous solution, extremely sensitive to heat, being converted into the above-mentioned viscid products, that an explanation was forthcoming. So quickly does this transformation occur that the acids cannot even be crystallised unchanged from hot aqueous solution, as has hitherto been the custom. On attempting to recrystallise a quantity of the pure substance from water, only 40 per cent. was recovered, and, moreover, its melting point was 10° lower than when crystallised from other solvents.

By carefully avoiding anything more than the slightest warmth when dealing with aqueous solutions of the acids, the two structural isomerides were satisfactorily isolated. They were isolated by taking advantage of their different solubilities in water and in chloroform. The less soluble methylsuccinanilic acid melts at 159°, and is the main constituent of Anschütz's acid melting at 143°. Its isomeride is much more soluble both in water and in chloroform, and melts at 123°. Both acids, on being heated above their melting points, lose water, and are converted into methylsuccinimide.

No solution has been arrived at of the problem as to which of the acids the constitution

$$CH_3 \cdot CH(CH_2 \cdot CO_2H) \cdot CO \cdot NH \cdot C_6H_5$$

must be assigned, and to which the alternative

$$CH_3 \cdot CH(CO_2H) \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_5.$$
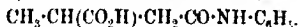
The matter is closely dependent on the constitution of the mesaconanilic acid which, on reduction, yields the methylsuccinanilic acid melting at 159° (Anschütz, *Ber.*, 1890, **23**, 891). Basing an argument on an erroneous observation of Reissert (*Ber.*, 1885, 2, 1370) on the oxidation products of mesaconanilic acid, Anschütz ascribed the constitution (I) to this acid, and, consequently, the constitution (II) to his methylsuccinanilic acid melting at 143° (*Annalen*, 1888, **246**, 117):
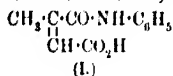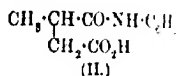
$$CH_3 \cdot C \cdot CO \cdot NH \cdot C_6H_5 \qquad CH_3 \cdot CH \cdot CO \cdot NH \cdot C_6H_5$$
$$ CH \cdot CO_2H \qquad\qquad\qquad CH_2 \cdot CO_2H$$
$$\qquad (I.) \qquad\qquad\qquad\qquad (II.)$$

Nevertheless, after revising Reissert's work, he convinced himself that no light whatever could be thrown on the constitution of mesaconanilic acid, or of methylsuccinanilic acid, as the result of oxidation experiments (*Ber.*, 1889, **22**, 747; and *Annalen*, 1889, **254**, 137).

It is noteworthy that during the whole of the controversy on these anilic acids between Reissert and Anschütz, the melting point, 143°, of methylsuccinanilic acid was not challenged by either of them. During this present investigation specimens of this substance, crystallised from water, have been obtained, melting at 143—145°, and having all the appearance of individual substances. In the first place, many of Anschütz's melting points are somewhat low, as has been pointed out by Auwers, owing to the very method of heating which he employed, whereby an incipient decomposition of the anilic acid sets in at temperatures below the true melting point. Secondly, these anilic acids should not be crystallised from water, for although succinanilic acid itself seems to be but little affected, yet others are rapidly attacked. Methylsuccinanilic acid (m. p. 159°), for example, has never been obtained

ꞁe crystallisation from water with a melting point higher than
ꞁ—150°.

ꞁꞁe only way open for the preparation of the neutral amides
ꞁꞁcinic acid and its homologues is by the action of ammonia
ꞁꞁe esters. Other methods lead either to the formation of a
ꞁꞁ preponderance of the unsymmetrical amide (this vol., p. 1737)
ꞁꞁ the imide. The rate of formation of the amides from the
ꞁꞁs and the percentage yield obtained has been found to depend
ꞁꞁe ester used and on the extent of substitution in the methylene
ꞁꞁs adjacent to the carboxyl, on spatial influence in other
ꞁꞁs. The methyl esters react much more quickly than the ethyl
ꞁꞁs, although the yield is about the same in each case. With
ꞁꞁstituted methylene groups, that is, with succinic ester itself,
ꞁꞁaction proceeds the most rapidly, and the introduction of
ꞁꞁyl groups produces a marked decrease, not only in the velocity
ꞁꞁrmation, but also in the yield. The reaction has been carried
ꞁꞁ a number of different ways for the sake of comparison,
ꞁꞁ the methyl and ethyl esters at ordinary and at elevated
ꞁꞁeratures, and the most satisfactory results have invariably
ꞁꞁ obtained by allowing the methyl esters to react at the ordinary
ꞁꞁerature with concentrated aqueous ammonia, but instead
ꞁꞁwing the liquids to remain in two layers, or using a shaking
ꞁꞁne just sufficient alcohol was added to bring the ester into
ꞁꞁn. In the succinic series this method has given better
ꞁꞁ than E. Fischer's process, devised for the malonic series,
ꞁꞁch the ethyl esters are heated with alcoholic ammonia in
ꞁꞁed tube at 130°, generally for twenty-six hours (Ber., 1902,
ꞁꞁ). A comparison of the results obtained in the various
ꞁꞁents, combined with Fischer's results in the malonic series,
ꞁꞁresting:

Acid.	Percentage yield of amide using alcoholic ammonia in bomb.		Percentage yield of amide using aqueous ammonia in cold.	
	Methyl ester.	Ethyl ester.	Methyl ester.	Ethyl ester.
ꞁ........................	—	98		
ꞁꞁmalonic	---	40	. .	. .
ꞁalonic	—	53	.....	.
ꞁꞁmalonic	---	61	.....	..
ꞁꞁylmalonic	----	2·6	. .	..
ꞁꞁbalonic	- -	0·0	. .	...
ꞁꞁ	63	40	80 (3 days)	80 (12 days)
ꞁꞁuccinic	33	.	52 (5 ,,)	...
ꞁꞁ-Dimethylsuccinic .	----	.	5 (30 ,,)	....
ꞁꞁmethylsuccinic	—		2 (30 ,,)	...

ꞁ yield of amide in the case of succinic acid is therefore com-
ꞁꞁ with that obtained with methylmalonic acid, and the sub-

stitution of one only of the four methylene hydrogen atoms in a methyl group produces a marked retardation in velocity and diminution in yield. Fischer suggested (*loc. cit.*) that the reaction with tetramethylsuccinic acid would probably yield only a trace of amide, but it is now evident that this is already the case with dimethylsuccinic acids, the amides of which have now been prepared for the first time. These results, whilst quite in harmony with Fischer's hypothesis that the methylene hydrogen is involved in a reaction in the formation of a preliminary ammonia addition product, or salt, of the type (III) which decomposes into

$$CO_2Et \cdot CMe \colon C(OEt) \cdot ONH_4 \longrightarrow CO_2Et \cdot CHMe \cdot CO \cdot NH_2$$
$$\text{(III.)} \qquad\qquad\qquad \text{(IV.)}$$
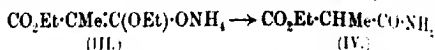
amide (IV), yet show that steric hindrance must be an important factor in the case, for there are still in the dimethylsuccinic acid two methylene hydrogen atoms similar to the one in methylsuccinic acid, yet the velocity of the amide-formation and the yield of amide are enormously greater in the latter case, whereas if the presence of an unsubstituted methylene hydrogen atom were the sole conditioning factor we should expect the acids to behave similarly, or at least that more than mere traces of dimethylsuccinamide were produced. Moreover, the results with the constitutionally isomeric *cis-* and *trans-*dimethylsuccinic acids are different, the *cis*-acid reacting more slowly than the *trans*-acid, as one would expect from considerations of spatial interference. The conclusion is therefore drawn that the accumulation of substituent groups round an esterified carboxyl group hinders the reaction with ammonia, even although some methylene hydrogen is still unsubstituted.

Experimental.

Succinanilide.

Succinanilide was obtained by Menschutkin (*Annalen*, **162**, 187) in 25 per cent. yield by the direct action of aniline on succinic acid. It can be obtained in better yield by the action of succinyl chloride on a solution of aniline in benzene (compare this vol., p. 1736, and Dunlop and Cummer, *J. Amer. Chem. Soc.*, 1903, **25**, 612). Since this method involves the previous production of succinyl chloride, which is itself obtained at most in 50 per cent. yield, the following direct method of preparation from the acid is preferred.

Twenty grams of succinic acid were heated for three to four hours at 200° (thermometer in the liquid) with 40 grams of aniline. A very short reflux air-condenser was used, so that only the aniline was condensed, the water generated by the reaction being allowed

escape, as it was found that if condensed and returned to the ... the temperature of the boiling mixture eventually sank as ... 125°, and the unsatisfactory yield described by Menschutkin ... obtained. The product was poured into dilute acid, and when ... the precipitate of anilide and anil was collected and warmed ... an excess of dilute aqueous sodium hydroxide, whereby the ... was dissolved as sodium succinanilate, but the amilide was ... attacked The latter was collected, and after one crystallisation ... alcohol was quite pure. From the aqueous solution of the ... succinanilate dilute hydrochloric acid precipitated succinanilic acid ... as almost pure condition. The above amount of succinic acid ... 19 grams of anilide and 25 grams of anilic acid, an almost ... theoretical yield.

Succinanilide crystallises from alcohol in short, stout needles, melting at 230° (Menschutkin gives 227°). It is quite insoluble in water, and is not acted on by boiling dilute alkali hydroxide. It is soluble in about 35 parts of boiling alcohol, and 460 parts at 16°, and almost insoluble in the other common organic solvents.

Conversion of Succinanilic Acid into Succinanilide.

The anilic acid obtained as a by-product in the above preparation is readily converted into the anilide by heating with 75 per cent. of its weight of aniline in sealed tubes at 110—115° for forty-eight hours. The product is a mixture of anilide and anil with some of aniline, similar to that obtained in the direct preparation, the anilide is separated by treatment with hydrochloric acid and then with sodium hydroxide exactly as there described. From grams of anilic acid 12 grams of anilide were obtained, and grams of anilic acid recovered (compare Tingle and Cram, Amer. ... J., 1907, 37, 597, who obtained only a 25 per cent. yield after five days' heating in an open vessel). By repeating this process with the recovered anilic acid it is eventually almost wholly transformed, giving a total yield of about 30 grams of succinanilide from the 20 grams of succinic acid originally taken.

Methylsuccinanilide.

This has been briefly described in a previous paper (this vol., 1361). Unlike succinanilide, it could be obtained only in traces the action of aniline on either the free methylsuccinic acid or anilic acid. Under all experimental conditions tried, ring formation ensued with the almost exclusive production of the anil. contrast with succinanilide it is very readily soluble in alcohol, fairly soluble in ethyl acetate, sparingly so in chloroform, and soluble in water or benzene.

Methylsuccinanil.

This was obtained in almost theoretical yield by an improvement of Kling's process (*Ber.*, 1897, **30**, 3040). Ten grams of methyl-succinic acid were gently boiled for a few minutes with ½ gram of aniline in an inverted retort. The retort was then reversed and the mixture distilled as rapidly as possible. No appreciable carbonisation occurred, and the distillate solidified to a mass of the anil, which after one crystallisation from much boiling water formed clusters of tiny needles melting at 109—110° (Klason gives 104°, and Kling 107°).

Methylsuccinanil is very readily soluble in alcohol, ethyl acetate, chloroform, or benzene. It is soluble in about 40 parts of boiling water, and to the extent of 0·28 per cent. in water at 16°.

Methylsuccinanilic Acids.

An aqueous solution of the sodium salts of the two isomerides was prepared either by dissolving the product of the action of aniline on methylsuccinic anhydride in cold sodium hydroxide solution, or methylsuccinanil in aqueous sodium hydroxide by the aid of gentle heat. The isolation of the two isomerides was accomplished by fractional precipitation of the acids from this solution combined with fractional crystallisation from chloroform. In one experiment 7·7 grams of methylsuccinanil were dissolved in 50 c.c. of 2N-sodium hydroxide, and to the filtered solution hydrochloric acid was slowly added with constant agitation. No oil was precipitated, but a clear solution was obtained, from which in a few moments crystals of the anilic acid separated. The following fractions were obtained: (1) After the addition of 20 c.c. of 2N-hydrochloric acid 1·9 grams were deposited, melting at 155°, which, when recrystallised twice from ethyl acetate, melted at 158—159°. (2) On adding a further 10 c.c. of 2N-hydrochloric acid, 2·8 grams were deposited, melting at 95—135°, which, when extracted with cold chloroform. The residue (1·3 grams) consisted of the acid melting at 159°, and after crystallisation from ethyl acetate melted at this temperature. The solution contained most of the isomeric acid, and it was added to the chloroform solution (see below). (3) On keeping overnight, 1·0 gram of material separated, melting at 85—95°. This was the fairly pure isomeric acid, and was almost entirely soluble in cold chloroform.

The united chloroform solutions were precipitated with light petroleum, and the precipitate (m. p. 105—108°) was purified by a process of alternate precipitation from the aqueous solution of its sodium salt, and recrystallisation from chloroform. This gave

, successful because the difference in the solubility of the iso-
meric in water was not so great as in chloroform. Eventually a
product was obtained melting at 123°, which consisted of broad,
as-cut, microscopic needles, and further treatment produced no
alteration in the melting point.

The less soluble acid appeared to form from 40 to 45 per cent.
the total product, but, of course, the more soluble acid could
not be isolated in a pure condition in quantity anywhere
reaching the amount (55—60 per cent.) in which it was
present.

In order to remove all doubt as to the chemical individuality
these two acids, the following data were obtained.

Methylsuccinanilic acid, m. p. 159°, crystallises from ethyl
acetate in fairly broad, flat needles. It is very readily soluble in
alcohol, moderately so in ethyl acetate, and very sparingly so in
chloroform (about 0·05 per cent. at 18°) or water (0·09 per cent.
at). When heated above its melting point it is converted into
anil, melting at 109°:

0·341 gave 0·2361 CO_2 and 0·0597 H_2O. C = 63·69; H = 6·56.
0·166 ,, 9·2 c.c. N_2 at 15° and 749 mm. N = 6·85.

$C_{11}H_{13}O_3N$ requires C = 63·76; H = 6·28; N = 6·76 per cent.

Methylsuccinanilic acid, m. p. 123°, crystallises from chloroform
, broad, microscopic needles. It is extremely readily soluble
alcohol or ethyl acetate, very readily so in hot chloroform, and
chloroform solution contains 1·6 per cent. at 16°. It is fairly
readily soluble in hot benzene, insoluble in light petroleum, and
moderately soluble in water (1·2 per cent. at 15°). When heated
to its melting point it is converted into the anil melting at 109°,
a mixture with the anilic acid melting at 159° melted at 105—108°,
when this mixture was recrystallised fern-like clusters of the
mixture type were obtained:

0·357 gave 0·2225 CO_2 and 0·0554 H_2O. C = 63·43; H = 6·43.
0·294 ,, 7·1 c.c. N_2 at 16° and 760 mm. N = 6·94.

$C_{11}H_{13}O_3N$ requires C = 63·76; H = 6·28; N = 6·76 per cent.

Succinamide.

This compound can be obtained only in minute quantity by the
action of ammonia on succinyl chloride. It was prepared, however,
a variety of ways indicated in the introductory portion, and in
per cent. yield by the action of concentrated aqueous ammonia
methyl succinate, just sufficient alcohol being added to the
mixture to bring the ester into solution. After three days the
action was complete, and the precipitated amide was found to be

almost pure without further treatment. It crystallises from hot water in short, stout needles, melting and decomposing at 223°. This is considerably higher than the melting point usually given, and if the temperature rises slowly a much lower value is usually obtained. One part of the amide dissolves in 15 parts of boiling water, and in 300 parts of water at 15°. It is almost insoluble in alcohol and other organic solvents.

Methylsuccinamide.

This was prepared most readily in the same way as succinamide, by the action of concentrated aqueous ammonia on a solution of the methyl ester of the acid. After remaining for five days at the ordinary temperature no more amide was deposited, and the total yield then amounted to 52 per cent. of the theoretical. Methylsuccinamide crystallises from water in short needles, melting and decomposing at 225°. It is almost insoluble in alcohol and other solvents, but soluble in about 50 parts of water at 15°, and is very soluble in hot water.

cis- and trans-Dimethylsuccinamide.

[With SIDNEY HENRY GROENEWOUD.]

The only mention of a dimethylsuccinamide in the literature is by E. von Meyer (*J. pr. Chem.*, 1882, [ii], **26**, 359), who states that he prepared it by the action of ammonia on the oily product obtained by the bromination of cyanethine. The salt is described as crystallising in fine, pyramidal, pointed prisms, and did not melt at 260°. That it could really have possessed the constitution assigned to it by von Meyer seems impossible, as these properties agree in no way with those of either the *cis*- or trans-amide obtained by a method which admits of no doubt, namely, from the respective esters by the action of ammonia. It seems, moreover, improbable that the symmetrical amides could be obtained in any appreciable quantity by the action of ammonia on the acid bromides, even if such were present in the oil obtained from cyanethine.

cis-*Dimethylsuccinamide* was obtained by the action of concentrated aqueous ammonia on dimethyl *cis*-dimethylsuccinate (m. p. 200°), prepared according to Zelinski's method (*Ber.*, 1891, 24, 646), sufficient alcohol being added to make the alcoholic strength of the resulting solution about 33 per cent. After being kept for one month at the ordinary temperature 0·06 gram of amide separated in well-formed, triclinic prisms from a solution containing 3 grams of the ester. The mother liquors yielded on evaporation

...al consisting apparently in the main of unchanged ester, but treating this a second time with ammonia no less than 0·6 gram crystals separated in fourteen days. The crystals obtained by these operations, after washing with alcohol, were quite pure without other treatment. They melted and decomposed at 244°, and were insoluble in alcohol or cold water, but fairly readily soluble in water:

...·651 gave 16 c.c. N_2 at 22° and 767 mm. N = 19·49.

$$C_6H_{12}O_2N_2 \text{ requires } N = 19·44 \text{ per cent.}$$

trans-*Dimethylsuccinamide* was obtained in a precisely analogous manner to the *cis*-amide by substituting the *trans-* for the *cis*-methyl ester in the experiment described above. Under similar conditions 3 grams of the *trans*-ester yielded a larger amount of amide in the first treatment, namely, 0·15 gram. It was deposited in minute prisms of similar appearance, and solubilities in alcohol and water, as the *cis*-isomeride. It melted and decomposed at 238°:

...·695 gave 18·6 c.c. N_2 at 20° and 760 mm. N = 19·63.

$$C_6H_{12}O_2N_2 \text{ requires } N = 19·44 \text{ per cent.}$$

Both amides were decomposed extremely slowly by boiling hydrochloric acid, more rapidly by boiling potassium hydroxide solution. Unfortunately the quantities at our disposal were too small for the purification products to be satisfactorily identified, but since the amides regenerated their corresponding acids on hydrolysis and it is extremely improbable that the action of cold ammonia would cause any change of configuration, it may be confidently assumed that the amides, also, yield on hydrolysis the respective acids from which they were obtained.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C.

CCLIII.—*A Magnetic Study of Compounds of Water and of Aqueous Solutions.*

By FRANCIS WILLIAM GRAY and WILLIAM MILNE BIRSE.

THE object of the work described in the present paper was to ascertain whether magnetic measurements can throw any light on the state of combination of water in compounds of different types, and especially to measure the magnetic properties of water in (1) aqueous salt solutions, (2) hydrated crystals such as those of zinc sulphate, and (3) organic acids, such as benzoic and oxalic acids, which may be regarded as compounds of their anhydrides with water.

In all these classes instances were found in which the additivity, in the molecular sense, is obeyed. Thus aqueous solutions of potassium ferricyanide obey the law of additivity throughout the whole range of concentration, and yield a more trustworthy value for the susceptibility of potassium ferricyanide than is obtained from the solid.

In the case of copper sulphate, if it is assumed that the susceptibility of the water is not affected appreciably by the union, it is found that the paramagnetic susceptibility of the anhydrous copper sulphate molecule is increased by about 11·5 per cent. as it unites with one molecule of water. Further addition of water molecules to form the higher hydrate has no marked influence on the susceptibility.*

In the case of organic acids it is found that additivity, in a molecular sense, holds for benzoic, phthalic, maleic, and oxalic acids, but not for succinic and camphoric acids.

Aqueous solutions of potassium ferricyanide obey (see later) very nearly the equation $\frac{x}{10\cdot07} - \frac{y}{0\cdot72} = 1$, where x = the weight of potassium ferricyanide in 100 grams of aqueous solution, and $y \times 10^{-6}$ denotes the susceptibility of a solution of percentage x. It is not usual for an aqueous solution to follow so closely the additive law. Indeed, many of the older determinations of the susceptibility of salts are quite valueless, since they were obtained from determinations of solutions of single concentrations on the basis of additivity, and the value obtained in this way varies usually according to the concentration of the solution. Cabré and Moles (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 425) have shown how the atomic susceptibility of iron varies with the concentration in solutions of ferric chloride, ferric nitrate, and sodium iron pyrophosphate.

In the magnetic study of solutions the following effects are to be looked for: (1) ionisation, (2) union of two or more molecular magnets to yield an astatic system not oriented in a magnetic field, (3) formation of hydrates and the stability of the same, (4) hydrolysis. In addition, care must be taken to ascertain whether or not the susceptibility of a solution changes with time. Instances have been found of solutions originally additive which showed a gradual departure from additivity. Heydweiller (*Ber. Deut. physikal. Ges.*, 1913, **15**, 112) gives results for solutions of ferric chloride, manganese sulphate, and nitrate, nickel nitrate, chromic sulphate, chromic nitrate, and cobalt nitrate. He observed a maximum in the curves for the relation between concentration and molecular

* It is well known that similar differences have been observed in the specific heats and heats of hydration for the different water molecules in polyhydrates.

sibility. This maximum may be produced by the joint action
fect (1), which causes increase of susceptibility, and effect (2),
a causes diminution of susceptibility. Oxley discusses effect (3)
Camb. Phil. Soc., 1912, **16**, 421), and points out that the
rate may be so unstable as not to affect the magnetic properties
g Wiedemann claims from magnetic measurements to be able
calculate the degree of hydrolysis of ferric chloride in aqueous
tions. In aqueous solutions of potassium ferricyanide which
t to obey the additive law none of the above effects can be
cted by the present method.

ang $\frac{x}{10\cdot07} - \frac{y}{0\cdot72} = 1$ and putting $x = 100$, we obtain for the sus-

bility of potassium ferricyanide the value $+6\cdot43 \times 10^{-6}$. This
s 10·97, or very nearly 11 magnetons per molecule. Weiss
gt. rend., 1911, **152**, 367) gives 10·41 magnetons.

se susceptibility of solid potassium ferricyanide (powder) was
d to be $+6\cdot77 \times 10^{-6}$, the error-range being $\pm0\cdot16$, or about
per cent. (when calculated by the average deviation method).
figure, 6·77, gives 11·26 magnetons per molecule.

sle (*Ann. Physik*, 1913, [iv], **41**, 829) points out, in the case
diamagnetic powders, that the molecules at the surface of the
s are most easily oriented in the magnetic field. An increase
se size of the particles causes a diminution in the total surface,
therefore in the number of surface molecules, and thus a fall
te susceptibility. This was found to hold for powdered potass
ferricyanide.

s the other hand, the increased density which accompanies
used size of particles tends to an increased value for the
ptibility.

s the whole, therefore, with potassium ferricyanide, the sus
bility obtained from solutions is more trustworthy than that
s powders, because with solutions the precision is much better,
law of additivity is obeyed throughout the whole range of
estrations, and, further, the result implies an integral number
agnetons per molecule.

s order to account for the magnetic difference between copper
ate monohydrate and copper sulphate pentahydrate, we
set the following hypothesis: that the water-molecules are
sged in space round the outside of the copper sulphate molecule,
s the vicinity of each oxygen atom and one in the vicinity
te copper atom. The last-mentioned water-molecule is the only
that causes deviation from the additivity of the magnetic
perties. When two copper atoms of two anhydrous copper
ate molecules are near one another they hamper one another's
ement in the magnetic field. Thus the orientation of the copper

atom is not so free in the anhydride as in the monohydrate, as in the pentahydrate, in both of which water-molecules intervene between the copper atoms, keeping them apart and thus preventing the mutual action above referred to. In other words, the mean magnetic susceptibility of the copper atom is less in the anhydride than in the monohydrate or in the pentahydrate.

This theory receives support from the fact that similar hypotheses have served to explain two observations recently made in the cryogenic laboratory at Leiden. Perrier and Onnes (*Compt. rend.*, 1914, **158**, 941) studied mixtures of liquid oxygen and nitrogen, and found that the coefficient of magnetic susceptibility of liquid oxygen increases as the concentration diminishes. Again Onnes and Oosterhuis (*Proc. K. Akad. Wetensch., Amsterdam*, 1913, **15**, 969) in studying paramagnetism at low temperatures found for hydrates of salts and anhydrous salts, in the case of ferrous sulphate and manganese sulphate, that whilst the hydrate obeyed Curie's law, $\chi T = $ constant, down to the temperature of liquid nitrogen, the anhydrous salt followed the law, $\chi (T + \Delta) = $ constant, where $\chi = $ specific susceptibility, $T = $ absolute temperature, and $\Delta = $ a constant. Thus, at any given temperature within a certain range the paramagnetism is increased by the union of water with the salt.

Mlle. Feytis (*Compt. rend.*, 1911, **153**, 668) about the same time as we made our observations obtained similar results for copper sulphate (see experimental part).

Mlle. Feytis (*loc. cit.* and *Compt. rend.*, 1913, **156**, ...) for the salts $CuCl_2,2H_2O$, $CuCl_2,2NH_4Cl,2H_2O$, $CuCl_2KCl,H_2O$, and $NiSO_4,6H_2O$ departure from additivity in the same sense as copper sulphate. On the other hand, she observed that additivity held for the salts $CoSO_4,7H_2O$, $Cr_2(SO_4)_3,16·74H_2O$, and

$$K_2SO_4,Cr_2(SO_4)_3,24H_2O,$$
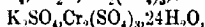
but not for $CrCl_3,6H_2O$, for which the departure was in a direction opposite to that for copper sulphate. This last case may be brought into line with our hypothesis by supposing that in anhydrous chromic chloride the chlorine atoms are arranged symmetrically round the chromium atom, chlorine atoms keeping apart the chromium atoms of different salt molecules, and thus enhancing the paramagnetism. When water unites with the anhydrous salt we suppose that there is no longer the symmetry referred to, so that chromium atoms can come nearer one another than before, and thus the atomic paramagnetism of the chromium is diminished. The hydrates of chromic chloride are represented thus:
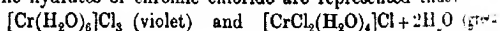
$[Cr(H_2O)_6]Cl_3$ (violet) and $[CrCl_2(H_2O)_4]Cl + 2H_2O$ (green). The difference between these is not shown in magnetic measurements.

we have observed departure from additivity in the hydrates of magnetic salts also, and from our own results and those of others have been led to the general rule, that when there is departure in additivity a paramagnetic anhydride has its paramagnetism raised and a diamagnetic anhydride has its diamagnetism raised by the union with water, on the assumption that the susceptibility of the water is not affected appreciably by the union. A paramagnetic substance the always present diamagnetism is ruled by the larger paramagnetism. According to our general rule the diamagnetism in a paramagnetic substance might be raised by union with water (when there is departure from additivity), and thus the apparent paramagnetism would be raised. We believe, however, that the departure from additivity in paramagnetic salts can be only partly explained by this cause, and that the hypothesis suggested under copper sulphate, or a substitute, is still required.

For copper sulphate pentahydrate the theory might be brought forward that the water of crystallisation is made up of two dihydrol molecules and one monohydrol molecule, or one trihydrol molecule and two monohydrol molecules, or one trihydrol molecule and one dihydrol molecule, or one dihydrol molecule and three monohydrol molecules, or five monohydrol molecules. The first of these five possibilities is best suited for explaining how one water-molecule differs from the other four. We think, however, that this would account for only a very small magnetic difference, judging from the results of Piccard (Compt. rend., 1912, **155**, 1497), who studied the susceptibility of water at various temperatures from 0° to 100°. The susceptibility of water is only 0·75 per cent. greater at 100° than at 0°; also the decrease on solidification is 2·4 per cent., so that variations in the proportions of trihydrol, dihydrol, and mono-hydrol has very little effect on the susceptibility.

Similarly the results of Piccard do not encourage us to suppose that departure from additivity in a hydrate is due to any appreciable extent to any change in the magnetic susceptibility of the water, that is, to change caused by the union with the anhydride.

The water which is present in a paramagnetic metallic hydroxide is usually regarded as a clear case of water of constitution, and as water unites with the oxide to form the hydroxide there is also a considerable enhancing of the paramagnetic susceptibility of the oxide molecule. Thus, there are hydrates and hydroxides in which the magnetic rôle of water is identical, and it becomes an interesting question whether we can extend the hypothesis we have for hydrates to the case of metallic hydroxides.

With regard to the organic acids (see tables III and IV) the parallelism between constitutional and magnetic similarities and

differences is interesting.   In every case except the two acids we
show decided departure from additivity (succinic and camphoric
acids), the anhydride is obtained from the interaction of the
carboxyl groups which are either near one another in the same
molecule or are in different molecules, so that interaction can take
place without any great change in the configuration of the atoms
and their electrons.   On the other hand, with succinic acid there is
a marked change in the relative position of the atoms when the two
carboxyl groups at the ends of the open chain interact to form the
cyclic compound, and similarly with camphoric acid where two
carboxyl groups attached to two non-adjacent carbon atoms of the
camphoceanic ring interact to give the anhydride.

In comparing our results with Pascal's it should be noted that
we use for the molecular susceptibility of water the experimental
value $-12{\cdot}96 \times 10^{-6}$, whilst the sum of Pascal's atomic values is
$-10{\cdot}46 \times 10^{-6}$.   In calculating the molecular susceptibility of an
organic compound, however, Pascal introduces corrections for con-
stitution, so that the two methods are not necessarily the same.
At any rate, our experimental figures and Pascal's calculated ones
agree for fumaric acid and maleic acid and benzene; also accord-
ing to our method, additivity holds for these three substances.

EXPERIMENTAL.

The recent concordant results of de Haas and Drapier (?),
of Weiss and Piccard (1913), and of Sève (1912) yield for the
specific susceptibility of water reduced to a vacuum the value
$-0{\cdot}72 \times 10^{-6}$, which we use here in preference to the value
$-0{\cdot}75 \times 10^{-6}$ formerly used by Pascal, and the still older value
of Curie, namely, $-0{\cdot}79 \times 10^{-6}$.

All our results were obtained with a Curie-Chéneveau mag-
balance except number 8 of table III, for which a Pascal balance
was used.   The permanent magnet of the Curie-Chéneveau balance
had an average field of 232 gauss per sq. cm. over an area
$5{\cdot}6$ sq. cm. round and at right angles to the axis.   Plain
torsion wires were used about 33 cm. long and of diameter
mm., $0{\cdot}10$ mm., or $0{\cdot}07$ mm., according to the requirements.   The
scale was placed at a distance of more than 2 metres from the
mirror.   The greatest precision was obtained with a pure liquid,
for example, with benzene, as shown in table III.   All the solids
in table III were in the form of powder, and the precision was
usually not so great as with benzene.   In some cases we improved
the precision by heating the anhydride both before and after it was
in the tube, or by leaving the filled tube in a vacuum desiccator for
some time before the determination.   With a glass tube the heat
might cause volume changes resulting in error, and it occurred

try a quartz tube.[4] We found, however, that little, if any, ... was gained by its use, as the susceptibility of the quartz was ... greater than that of the glass we used, so that a degree of ... certainty was introduced which perhaps more than balanced ... advantage obtained from the constancy of volume of the quartz. In the case of the substances in table IV we sometimes found ... purification improved the precision, even when the method of ... cation produced no change in the melting point

Result number 8 in table III was obtained with a Pascal balance, ... field of the electromagnet having an average of about 9000 ... per sq. cm. over an area of 2·21 sq. cm. at right angles to ... round the axis.

The determinations were carried out at 15°.

In the following numerical results we have given as many digits ... are obtained in our calculation. The precision of the estimation ... cates how many digits should be retained in each case.

Magnetic Susceptibility of Aqueous Solutions of Potassium Ferricyanide.

TABLE I.

Substance or number.	Number of measurements.	x.	y.	y_1.	d_1.	y_2.	d_2
A	3	29·13	+1·394	+1·362	+0·032	+1·354	+0·040
B	2	26·22	+1·188	+1·155	+0·033	+1·148	+0·040
C	3	23·53	+0·993	+0·962	+0·031	+0·956	+0·037
	2	20·35	+0·731	+0·735	−0·004	+0·731	0·000
	2	17·32	+0·513	+0·518	−0·005	+0·515	−0·002
	2	15·55	+0·391	+0·392	−0·001	+0·390	+0·001
	3	12·37	+0·162	+0·164	−0·002	+0·163	+0·001
	1	11·08	+0·0675	+0·0722	−0·0047	+0·0718	0·0043
	2	8·27	−0·123	−0·129	+0·006	−0·128	+0·005
	1	7·416	−0·178	−0·189	+0·011	−0·188	+0·010
	4	6·005	−0·286	−0·291	+0·005	−0·289	+0·003
	4	4·594	−0·383	−0·392	+0·009	−0·390	+0·007
	6	2·976	−0·506	−0·507	+0·001	−0·504	0·002

In table I, x denotes the weight of potassium ferricyanide in ... grams of aqueous solution, $y \times 10^{-6}$ denotes the susceptibility ... by experiment for a solution of percentage x. y_1 is the ... of y as obtained from $\dfrac{x}{10·07} - \dfrac{y}{6·72} = 1$. d_1 denotes the distance ... direction of y that the experimental point is above or below ... straight line; + means above, − means below. Under y_2 and ... are given corresponding values obtained from $\dfrac{x}{10·07} - \dfrac{y}{0·716} = 1$.

... ting the three solutions A, B, and C, we note that the first ... ght line fits the experimental points very closely, and that the ... line fits still closer, but does not pass through the water- ... However, taking into account the degree of uncertainty of

the measurements and seeing how near the lines lie to one another
we need not push the refinement of the calculation so far, and may
be content with the first and simpler equation.

Of the solutions, A was the most concentrated we could conveniently use, and its composition was found by chemical analysis.
By adding a weighed amount of A to a weighed amount of water,
B and C were obtained. S was prepared by adding a weighed
amount of water to a weighed amount of pure potassium
cyanide. A stock of S was prepared, from which, by the weighing
method, the series of solutions 1 . . . . 9 were obtained. Thus,
any error in the determination of the composition of A will affect the
B and C, and any error in the preparation of S will affect the
1 to . . . . 9. The two sets are, of course, independent of one another.
This explains why the three points obtained with A, B, and C
deviate further from the straight line than any of the points of the
set S, 1, ... 9. It is probable that the analysis by
chemical means is not so accurate as the preparation of S by the
weighing method.

The degree of the uncertainty of the magnetic measurements
of the solutions will be seen from solution 9, for which the greatest
deviation from the mean was $0·0038$ or $0·76$ per cent.

TABLE II.

Substance.	Specific susceptibility $\times 10^6$.		Average deviation from mean.		Molecular suscepti-bility 10^6	Nature of solutions.
	Mlle. Feytis' values.	Our values.	Abso-lute.	Per cent.		
$CuSO_4$	8·6	8·39	0·02	0·2	1339	
$CuSO_4,H_2O$	8·6	8·32	0·04	0·5	1479	
$CuSO_4,5H_2O$	5·9	5·81	0·03	0·5	1450	

Molecular susceptibility of $CuSO_4,H_2O$	1479 $\times 10^{-6}$
Correction for water	13
Susceptibility of the molecule $CuSO_4$ in $CuSO_4,H_2O$	1492 $\times 10^{-6}$
Molecular susceptibility of anhydrous $CuSO_4$	1339 $\times 10^{-6}$
Difference	153 $\times 10^{-6}$

Thus, the union with one molecule of water has increased the
paramagnetic susceptibility of the anhydrous copper sulphate molecule by $+153 \times 10^{-6}$ or by about $11·5$ per cent. Further addition
of water molecules to form the higher hydrate has no marked influence on the susceptibility.

Otherwise :

Substance.	Molecular susceptibility $\times 10^6$.		Deviation for additivity	
	Experimental.	Calculated.	Absolute.	Per cent.
$CuSO_4,H_2O$ ...	1479	$+1326$	153	
		(from $CuSO_4$ and H_2O)		
$CuSO_4,5H_2O$ ...	1450	$+1427$	23	
		(from $CuSO_4,H_2O$ and H_2O)		

Copper Nitroprusside.

	Specific suscep- tibility ×10⁶	Average deviation from mean		Number of measure- ments.	Molecular suscep- tibility ×10⁶	Deviation from additivity per cent.
		Abso- lute.	Per cent.			
Cu₃Fe(CN)₆,2H₂O	+4·54	0·05	1·0	5	+1432	8·4
Cu₃Fe(CN)₆	+5·73	0·03	0·5	5	+1593	—

This would indicate that the deviation is opposite in direction to that for copper sulphate. However, any slight decomposition in preparation would make the anhydride too highly paramagnetic. A general study of nitroprussides, on which we are at present engaged, may throw more light on this question.

Some Diamagnetic Salts.

Potassium ferrocyanide:

Molecular susceptibility of K₄Fe(CN)₆,3H₂O = −172·0×10⁻⁶
Correction for 3H₂O = − 38·9
Susceptibility of the molecule K₄Fe(CN)₆ in K₄Fe(CN)₆,3H₂O = −133·1
Molecular susceptibility of anhydrous K₄Fe(CN)₆ = −145·1
Difference 12.

On union with water the diamagnetism of the molecule K₄Fe(CN)₆ is diminished by about 9 per cent.

The following figures were calculated from the results of St. Meyer. Loss per cent. means the percentage by which the diamagnetic susceptibility of the anhydrous salt molecule is reduced by union with water to form the given hydrate.

Hydrate	MgCl₂,6H₂O.	CaCl₂,6H₂O	BaCl₂,2H₂O.
Loss per cent	over 100	over 100	25

Hydrate	MgSO₄,7H₂O.	Li₂SO₄,H₂O.	Na₂CO₃,10H₂O
Loss per cent	over 100	24	over 100

This would imply that in these salts we have paramagnetism masked by the diamagnetism of the water.

TABLE III.

Organic Acids.

Reference number. Substance.	Specific susceptibility ×10⁶	Average deviation from mean		Number of measure- ments.
		Absolute.	Per cent.	
1. Benzene	−0·7086	0·0049	0·7	5
2. Benzoic acid	−0·5560	0·0123	2·2	6
3. Benzoic anhydride	−0·5522	0·0060	1·1	6
4. Phthalic acid	−0·4878	0·0054	1·1	7
5. Phthalic anhydride	−0·4460	0·0048	1·1	6
6. Maleic acid	−0·4269	0·0182	4·0	8
7. Fumaric acid	−0·4158	0·0043	1·0	4
8. Fumaric acid	−0·4269	0·0095	2·2	5
9. Maleic anhydride	−0·3654	0·0056	1·5	6

TABLE III. (continued).

Reference number. Substance	Specific susceptibility $\times 10^6$.	Average deviation from mean.		χ as of substance
		Absolute.	Per cent.	
10. Succinic acid ...	0·4615	0·0015	0·3	
11. Succinic anhydride ...	−0·4753	0·0111	2·3	
12. Camphoric acid	−0·7461	0·0054	0·5	
13. Camphoric anhydride ...	−0·6294	0·0172	2·7	

TABLE IV.

Reference number. Substance.	Molecular susceptibility $\times 10^6$.		Deviation from additivity. Per cent.	
	Experimental.	For additivity.		
2. Benzoic acid...	67·78	−68·85	1·5	
3. Benzoic anhydride ...	62·37 × 2	—		
4. Phthalic acid...	−81·36	−78·97	2·5	
5. Phthalic anhydride ...	−66·01	—		
6. Maleic acid ...	−49·52	−48·77	1·5	
7. Fumaric acid...	−48·23	−48·77	1·0	
8. Fumaric acid ..	−49·52	−48·77	1·5	
9. Maleic anhydride ...	−35·81	—		
10. Succinic acid...	−54·45	−60·49	9·9	
11. Succinic anhydride ...	−47·53	− ·	·	
12. Camphoric acid	149·3	−125·3	19·0	
13. Camphoric anhydride ...	112·3	− ·	—	

	Molecular susceptibility $\times 10^6$	Pascal gives	
Benzene........................	−55·27	−55·1 (Expt.)	
Phthalic acid	−81·36		
Mean	−68·31		
Benzoic acid	−67·78		

Thus when the molecular susceptibility of benzoic acid is calculated from benzene and phthalic acid on the basis of additivity then the experimental result differs from this calculated value less than 1 per cent.

Under the heading " Pascal " we give the molecular susceptibilities as calculated from Pascal's atomic values and his correction for constitution.

PHYSICAL CHEMISTRY DEPARTMENT,
ABERDEEN UNIVERSITY.

Organic Chemistry.

Isoprene from Commercial Turpentines. CHAS. H. HERTY and D GRAHAM (*J. Ind. Eng. Chem.*, 1914, **6**, 803—804).—Ordinary oil turpentine yielded 5·5% of isoprene when submitted to distillation in "isoprene lamp" apparatus described by Harries and Gottlob (1911, i. 798); the fraction of oil of turpentine, b. p. 155—156°, had 8·0% of isoprene, and the fraction b. p. 160—175°, 0·5%. No prene was obtained from the fraction b. p. above 175°. It is evident the isoprene is derived from the pinene present. Oil of *Pinus* palustris yielded 12% of isoprene; pine oil, 4%; and refined spruce pine turpentine, none.

W. P. S.

Ethyl Ester of Linolic Acid Tetrabromide as a Product in Analysis of Cotton-seed Oil. LEROY S. PALMER and PHILIP WRIGHT (*J. Ind. Eng. Chem.*, 1914, **6**, 822—823).—During an investigation regarding the composition of cotton-seed oil, in which the saturated fatty acids were isolated by making use of their solubility ether, the authors obtained a crystalline compound, in place of the acid tetrabromide, when an attempt was made to form the latter above. The crystals had m. p. 58—58·5°, and consisted of ethyl late tetrabromide. The cause of the formation of this ethyl ester has been definitely ascertained, but it appears to take place during the the lead soaps are in contact with ether.

W. P. S.

Humic Acid. SVEN ODÉN (*Arkiv. Kem. Min. Geol.*, 1914, **5**, 5 Compare A., 1912, i, 336; this vol., i, 500).—When suspensions Sphagnum, Sphagnum peat and leaf humus are treated with ammonia, absorption of ammonia takes place, and, coincidently, salts are in considerable amounts from the peat and humus, whilst the gum itself gives only a relatively insignificant amount of salt. These results are opposed to the view of Baumann and Gully, who hold that the adsorption of bases by peat is mainly due to the use of *Sphagnum* cells. The effect on conductivity of the action of salts exceeds that of adsorption even in concentrations as N 0·005, so that the suggestion that humates are decomposition acts of the action of ammonia on humus is improbable.

With reference to the criticisms of Ehrenberg and Bahr (this vol., it is pointed out that filtration through collodion can only be used on when not less than 10% collodion is employed. It is also considered possible that as Ehrenberg and Bahr omitted to extract humic acid with alcohol, it may have contained a considerable of hymatomelanic acid which might account for the different obtained for the mol. weight.

N. H. J. M.

Isolation of Crystalline *dl*-Glyceraldehyde from a Syrup formed by the Oxidation of Glycerol. EDGAR J. WITZEMANN * Amer. Chem. Soc.*, 1914, **36**, 2223—2234).—The syrupy product

obtained by the oxidation of glycerol with hydrogen per..d
presence of ferrous sulphate (Fenton and Jackson, T., 1899, 7
contains *dl*-glyceraldehyde. This was established by convert...
aldehyde into the diethylacetal and recovering pure *dl*-glyceral
from the latter by hydrolysis with 0·1*N*-sulphuric acid.

Crystallised *l*-Mannose. W. ALBERDA VAN EKENSTEIN and
BLANKSMA (*Chem. Weekblad*, 1914, **11**, 902).—A yield of 1·5
l-mannose can be obtained by hydrolysis of the cyanohydr...
l-arabinose, isolation of mannonolactone from the mixture of t
nonic acid and *l*-gluconic acid, and reduction with sodium am...
To crystallise the sugar, it is converted into the phenylhydrazo...
then regenerated by the action of benzaldehyde. After several day
resulting syrup crystallises, and on recrystallisation from alcohol
colourless crystals, m. p. 132°.   It exhibits mutarotation, the in
rotation being [a]ᴅ +14°, and the final rotation [a]ᴅ +14°, in co...
agreement with the corresponding constants for *d*-mannose.

A J 1

Preparation of Raffinose. C. S. HUDSON and T. S. Ha
(*J. Amer. Chem. Soc.*, 1914, **36**, 2110—2114).—During a stud...
hydrolysis of raffinose by enzymes, a large quantity of the r...o
required.   A method for its preparation was therefore devis...
is superior to any of those hitherto recorded.

Cotton-seed meal is extracted with water, the aqueous so...
treated with basic lead acetate and filtered, and the filtrate treate
hydrogen sulphide to remove excess of lead, and again filter...
little sodium hyposulphite is added to prevent development of...
and the solution is boiled under reduced pressure until it becc
syrup containing about 25% of water.   Barium hydroxide is to a
and the barium raffinosate is powdered and washed with methy...
The barium compound is suspended in water and carefully dec...
with 50% phosphoric acid, so that the solution is exactly neutral a
end of this process.   After filtration, a little sulphuric acid is add
remove the last traces of barium, and the solution is again tha
treated for a few minutes with eponite (a form of vegetable char
filtered, and concentrated in a vacuum to a syrup containing 7°-
of water.   A small quantity of alcohol containing 0·3% of water
is added, and the mixture is seeded with crystals of raffinose and
and left at 0° to crystallise.   The crystalline mass is trit...
with 75% alcohol, filtered, and washed with alcohol of the
strength until the washings are colourless.   A yield of 4—5 of
weight of cotton-seed meal employed may thus be obtain...
colourless raffinose crystals.   The product may be further purifi...
recrystallisation.

E. F

The Solubility of Nitrocellulose in Mixtures of Ether
Alcohol. A. MATTEOSCHAT (*Chem. Zentr.*, 1914, i, 2095; from Z
ges. Schiess-Sprengstoffwesen, 1914, **9**, 105—106).—The auth
measured the solubility of a sample of gun-cotton in mixture
ether and dry or dilute alcohol. Absolute alcohol and ether is

portion 1 : 1 make a useful mixture, but with the common diluted spirits the proportion should be, ether to alcohol as 2 : 1 or 3 : 1.

J. C. W.

The Plurality of Amyloses. CH. TANRET (*Compt. rend.*, 1914, **159**, 530—533) —The author has determined the absolute and relative percentages of amyloses dissolved by water at different temperatures in different kinds of starch. For the starches used, water, at the same temperature, dissolves very different amounts of amylose. The results are a further proof of the plurality of amyloses as suggested by Bruisse and Roux.

W. G.

Metallic Compounds of Glycine. A. BERNARDI (*Gazzetta*, 1914, **44**, ii, 257—260).—The author has investigated the compound prepared by Dessaigne (*Annalen*, 1852, **82**, 365), examined later by Le and Kiesel (A., 1899, ii, 485), and known as mercury glycine, $[H_2CH_2CO_2]_2Hg$. It is found that the action of alkali on this compound results in no precipitation of mercuric oxide, but in the

formation of the compound $CH_2\!\!<^{NH->}_{CO\cdot O}\!\!>Hg$. It is suggested that

a latter compound be termed mercuriglycine, and the former named mercury aminoacetate.

Mercury aminoacetate, $(NH_2\cdot CH_2\cdot CO_2)_2Hg$, forms tufts of white needles, m. p. 110—111°. *Mercuriglycine*, $C_2H_3O_2NHg$, obtained by the use of the calculated proportion of calcium hydroxide solution on mercury aminoacetate, has m. p. 155° (decomp.), and when treated with sodium thiosulphate liberates sodium hydroxide quantitatively according to the equation :

$H_2O_2NHg + Na_2S_2O_3 + 2H_2O = CO_2H\cdot CH_2\cdot NH_2 + HgS_2O_3 + 2NaOH.$

As mercuric sulphate, mercury aminoacetate forms the double salt, $(CO_2\cdot CH_2\cdot NH_2)_2,HgSO_4,3H_2O$, decomp. 102°.

Calglycine, $CH_2\!\!<^{NH}_{CO_2}\!\!>Ca$, was also prepared.

T. H. P.

Three Isomeric Ethyl-*sec.*-butylhydroxylamines. LAUDER WILLIAM JONES and LEONORA NEUFFER (*J. Amer. Chem. Soc.*, 1914, **36**, 2202—2208).—Jones (A., 1907, i, 897) has described two isomeric hydroxylamines, namely, β-methyl-α-ethyl- and α-methyl-β-ethyl-hydroxylamine. In the present paper, an account is given of α-ethyl-β-butyl- and β-ethyl-α-*sec.*-butyl-hydroxylamines which are isomeric with β-ethyl-β-*sec.*-butylhydroxylamine (Bewad, A., 1900, i, 630 ; Lean and Goulding, T., 1901, **79**, 641).

When hydroxyurethane (carbethoxyhydroxamic) ethyl ether (Jones, 1898, i, 174) is treated with *sec.*-butyl iodide and sodium ethoxide, it is converted into *carbethoxy-α-ethyl-β-sec.-butylhydroxylamine (hydroxy-butylurethane ethyl ether)*, $C_4H_9\cdot N(OEt)\cdot CO_2Et$, b. p. 105—106·4°/ mm. On hydrolysing this compound with potassium hydroxide, it yields *α-ethyl-β-sec.-butylhydroxylamine*, $C_4H_9\cdot NH\cdot OEt$, b. p. 85—87°; its *hydrochloride* has m. p. 94°; the *platinichloride* was prepared and analysed.

By the action of *sec.*-butyl iodide on hydroxyurethane in presence of

potassium hydroxide, *carbethoxy-a-sec.-butylhydroxylamine* (*hydroxy-urethane sec.-butyl ether*), $CO_2Et\cdot NH\cdot O\cdot C_4H_9$, b. p. 116—127 mm., is produced, and this, on being treated with ethyl iodide sodium ethoxide, is converted into *carbethoxy-β-ethyl-a-sec.-butylhydroxylamine* (*hydroxyethylurethane sec.-butyl ether*),

$$C_4H_9\cdot O\cdot N Et\cdot CO_2Et,$$

b. p. 86·5—87°/30 mm. The latter compound, on hydrolysis, forms *β-ethyl-a-sec.-butylhydroxylamine*, $NHEt\cdot OC_4H_9$, b. p. 93·5—94°; *hydrochloride* is deliquescent; the *platinichloride* forms deep yellow crystals.

When carbethoxy-a-sec.-butylhydroxylamine is heated with potassium hydroxide, it is converted into a-sec.-*butylhydroxylamine*, $NH_2\cdot OC_4H_9$, b. p. 85·5°; its *hydrochloride* has m. p. 54·7—55°, and the *platinichloride* forms deep yellow crystals.

The carbethoxyhydroxylamines described in this paper are liquids with a characteristic odour; they do not reduce ammoniacal silver nitrate or Fehling's solution. a-sec.-Butylhydroxylamine, the ethyl-sec.-butylhydroxylamines have a characteristic aromatic odour; they reduce ammoniacal silver nitrate in the cold and Fehling's solution when heated.   L. D.

Some New Hydroxyurethanes and Chromoisomeric Silver Salts of Their Acyl Derivatives. LAUDER WILLIAM JONES and RALPH OESPER (*J. Amer. Chem. Soc.*, 1914, 36, 2208—2217). The experiments described in this paper were undertaken with a view to the preparation of mixed oximinocarbonic esters, $OR\cdot CNOR'$. Several new carbalkyloxyhydroxamic acids (hydroxyurethanes) have been obtained and their benzoyl esters studied. The silver salts of some of these benzoyl esters were obtained in two isomeric modifications, white and yellow, which are mutually transformable; methyl, ethyl, and isopropyl compounds yield only yellow salts, the isobutyl, isoamyl, and benzyl compounds furnish both modifications. When treated with alkyl haloids, these silver salts yield derivatives in which the alkyl groups are attached to nitrogen instead of oxygen, and for this reason the desired acyl derivatives of the oximinocarbonic esters could not be obtained.

Carbomethoxyhydroxamic acid, $OH\cdot NH\cdot CO_2Me$, was obtained as thick, yellow oil by the interaction of methyl chloroformate, hydroxylamine hydrochloride, and potassium carbonate. The *benzoyl ester* $OBz\cdot NH\cdot CO_2Me$, m. p. 82°, forms white needles; its *silver salt* $OBz\cdot NAg\cdot CO_2Me$, has m. p. 149—150°.

When the silver salt of the benzoyl ester of carbethoxyhydroxamic acid (Jones, A., 1898, i, 174) is heated, it becomes white at 150—153° then darkens rapidly, and melts at 174° (decomp.). The action of ethyl iodide and isoamyl iodide on this salt has already been described (this vol., i, 505). By the action of benzoyl chloride on the silver salt of carbethoxyhydroxamic acid or by the action of ethyl chlorocarbonate on the silver salt of dibenzhydroxamic acid, the dibenzoyl derivative of carbethoxyhydroxamic acid (A., 1898, i, 174) is produced.

Carbopropoxyhydroxamic acid, $OH\cdot NH\cdot CO_2Pr$, was obtained as thick, colourless oil. The *benzoyl ester* yields a *silver salt*, as

—145°, forming yellow needles which do not become white when cool. By the action of benzoyl chloride on this silver salt, the benzoyl derivative, $OBz\cdot NBz\cdot CO_2Pr$, m. p. 78—89°, is produced, and crystallises in cubes. When the silver salt is treated with ethyl iodide, the N-ethyl derivative, $OBz\cdot NEt\cdot CO_2Pr$, is obtained as a pale yellow oil, and is hydrolysed by hydrochloric acid with formation of propylhydroxylamine hydrochloride.

carbisobutoxyhydroxamic acid, $OH\cdot NH\cdot CO_2\cdot C_4H_9$, is a colourless oil. The benzoyl ester, m. p. 43—44°, yields a yellow *silver* salt which, when heated at 80—83°, is converted into a white modification, and has m. p. 158°. The N-ethyl derivative, $OBz\cdot NEt\cdot CO_2\cdot C_4H_9$, is a pale yellow oil.

carbisoamyloxyhydroxamic acid, $OH\cdot NH\cdot CO_2\cdot C_5H_{11}$, is a viscid, pale yellow oil. The benzoyl ester, a colourless oil, furnishes a yellow *silver* salt which becomes white at about 75° and melts at 141—142°. When this salt is treated with benzoyl chloride, the *dibenzoyl* derivative, $NBz\cdot CO_2\cdot C_5H_{11}$, m. p. 69—70°, is produced. The N-ethyl derivative, $OBz\cdot NEt\cdot CO_2\cdot C_5H_{11}$, is a pale yellow oil which yields amylhydroxylamine on hydrolysis.

carbobenzyloxyhydroxamic acid, $OH\cdot NH\cdot CO_2\cdot CH_2Ph$, has m. p. 65°. The benzoyl ester, m. p. 109—110°, yields a *silver* salt, m. p. 150—151°, which exists in yellow and white modifications. The N-ethyl derivative, $NEt\cdot CO_2\cdot CH_2Ph$, is a pale yellow oil.
E. G.

Syntheses in the Fluorene and Bisdiphenylene-ethylene Series. GONZALO GALLAS (*Anal. Fis. Quim.*, 1914, **12**, 112—131).—7-Dinitrofluorenone condenses with 2:7-dinitrofluorene at 160° in presence of zinc chloride to form 2:7:2′:7′-tetranitrobisdiphenyl-ethylene, which on reduction by means of tin and hydrochloric acid yields the corresponding *tetra-amino*-compound, colourless, silky needles, m. p. 250° (decomp.). The acid solution develops a blue coloration with oxidising agents.
G. D. L.

Action of Allylthiocarbimide on Various Amino-organic Compounds. G. ROSSI (*Gazzetta*, 1914, **44**, ii, 264—268).—In the absence of a solvent, the interaction of *o*-toluidine and allylthio-carbimide at the boiling point of the latter yields, not *s-o*-tolylallylthio-carbamide, but *s*-di-*o*-tolylthiocarbamide and allylamine.

The action of allylthiocarbimide on *o*-aminobenzoic acid is of a more elevated character and yields allyl cyanide, hydrogen sulphide, carbon dioxide and 3-nitrophthalanilide :
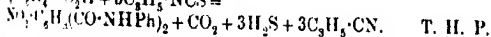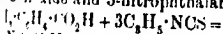
$C_6H_4\cdot CO_2H + 3C_3H_5\cdot NCS =$
$NO_2\cdot C_6H_3(CO\cdot NHPh)_2 + CO_2 + 3H_2S + 3C_3H_5\cdot CN.$
T. H. P.

Benzoylations in Ether Solution. WILLIAM M. DEHN and ALICE BALL (*J. Amer. Chem. Soc.*, 1914, **36**, 2091—2101).—In an earlier paper (Dehn, A., 1912, i, 833) an account was given of the action of acyl chloride on various bases in solution in dry ether. Similar experiments have now been carried out with benzoyl chloride and it has been found that, as with acetyl chloride, a mixture of the hydro-chloride and acyl chloride additive compound of the base is pre-

cipitated. In some cases, these precipitates are contaminated with the original bases or with their benzoyl derivatives. All the benzoyl chloride additive compounds are dissociated by water and many of them are unstable towards heat. The additive compounds of primary and secondary bases can generally be prepared by adding hydrogen chloride in ether or toluene solution to solutions of the benzoyl derivatives; the hydrochlorides of benzanilide, o-tolylbenzamide, and a-naphthylbenzamide, however, could not be obtained in this way.

*iso*Butylamine yields a mixture of its hydrochloride with *iso*butylbenzamide. The precipitate obtained with *iso*amylamine m. p. 201° and consists of *isoamylbenzamide hydrochloride*. *amylbenzamide* is an oil, b. p. 310—315°. Aniline gives a precipitate containing benzanilide and benzanilido hydrochloride. *p*-Toluidine yields *p*-tolylbenzamide and *p-tolylbenzamide hydrochloride*, and *m*-toluidine and a-naphthylamine afford mixtures of the trans chloride of the base, the benzamide, and the additive compound. Phenylhydrazine gives a precipitate consisting of phenylhydrazine hydrochloride, and benzoylphenylhydrazine and its *hydrochloride* Carbamide furnishes the additive *compound*, $CO(NH_2)_2 Bz'' = $ 209° (decomp.).

Diethylamine and methylaniline yield precipitates containing diethylbenzamide hydrochloride and phenylmethylbenzamide respectively. Piperidine furnishes *benzoylpiperidine hydrochloride*, which forms white, hygroscopic needles. Benzylethylamine gives *benzylethylbenzamide hydrochloride*; *benzylethylbenzamide* b.p. 218°/29 mm.

Additive *compounds* were also obtained with triethylamine, *iso*amylamine, dimethylaniline, diethylaniline, antipyrine, quinoline, pyridine, and a-picoline.

Copper Lakes of Eosin. HARVEY NICHOLAS GILBERT (*J. Amer. Chem.*, 1914, 18, 586—618).—An investigation has been made of a eosin copper lake with the object of ascertaining whether the substance is a definite compound or merely an adsorption complex consisting of copper hydroxide with the eosin adsorbed in approximately equal amount. It is shown that copper hydroxide, when treated with the solutions of eosin in varying quantities, exhibits the typical adsorption curve, and there is no indication of a chemical compound. In the amount of eosin taken up is about one-tenth of the amount required to form copper eosinate. Similar adsorption curves are obtained when magnesium oxide was shaken up with various eosin solutions. The composition of the copper lake produced by the interaction of copper sulphate and sodium eosinate was studied and was found that the precipitate contained an excess of copper in cases where an excess of copper salt was employed. It was also possible to synthesise lakes from copper hydroxide and eosin which behaved like the original lake. These lakes could be brought into colloidal solution, and all behaved similarly, although the ratio of copper to eosin varied from two molecules of copper to one of eosin to one molecule of copper to two of eosin. The amorphous lake has a

......ed into crystalline copper eosinate. The properties of the ...... lake differed entirely from those of the crystalline substance. ...... decomposition of the lake in aqueous suspension by means of ...... showed that the eosin was set free from the lake by the greater ...... traction of the copper hydroxide for the anions of certain salts. ...... anions are adsorbed by the copper hydroxide setting free the ...... sorbed eosin. The order of the decomposition, due to these adsorbed ...... is the same as is found for other cases of adsorption : $>$Br$>$Cl$>$NO$_3'$. The decomposition of the lake by aqueous alcohol ...... aqueous acetone is similar to that of ether and may be explained in ...... same way as due to the preferential adsorption of anions. The results ...... indicate that the lake, produced by the action of an aqueous ...... ation of sodium eosinate on a solution of copper sulphate, does not ...... sist of copper eosinate, although the copper and eosin are present ...... equivalent quantities. The lake consists of copper hydroxide, which ...... the method of formation contains an equivalent amount of ...... sorbed eosin. A colorimetric method for the estimation of eosin is ...... used, which consists in preparing a solution of cobalt nitrate of ...... exactly the same tint as a solution of eosin containing 0·00125 gram ...... litre. Such a cobalt solution contains 17·84 grams of the nitrate ...... litre. The method of estimation consists in diluting the given ...... solution until it has exactly the same tint as the cobalt standard.

<div align="right">J. F. S.</div>

p-Aminobenzaldehyde and Aniline. G. Rossi (*Gazzetta*, 1914, i, ii, 261—263).—The interaction of *p*-aminobenzaldehyde and ...... aniline yields *p*-aminobenzylideneaniline, which crystallises in ...... microscopic, canary-yellow needles, and forms a *picrate*, brick-red ...... exploding violently at 150°, and, when treated with ethyl ...... *p-ethyl aminobenzylideneaniline*, NHEt·C₆H₄·CH:NPh, red ...... cryst., decomp. 150°.

<div align="right">T. H. P.</div>

Oxidation of the Nopinine of Spanish Oil of Turpentine. ...... ROSIO MADINAVEITIA (*Anal. Fis. Quim.*, 1914, 12, 259—264).— ...... on oxidation with potassium permanganate in alkaline solution ...... nopic acid in conformity with the observations of Baeyer and of ...... (A., 1907, i, 936), and in opposition to the statements of ...... and Fernández (this vol., ii, 78).

<div align="right">G. D. L.</div>

Volatile Oil of Calycanthus floridus. EMERSON R. MILLER, W. TAYLOR, and M. H. ESKEW (*J. Amer. Chem. Soc.*, 1914, 36, 2...—2187).—The material used for this investigation consisted of the ...... of *Calycanthus floridus*, collected after the leaves had fallen. ...... were cut off just above the ground, freed from any remaining ...... allowed to dry in the air, and submitted to distillation with steam. Three samples of oil were obtained at different times in yields of 0·25%, and 0·39%; the small, young plants gave the best yield. ...... samples were pale yellow, soluble in all proportions in 90% alcohol, ... furnished the following constants: D_{25}^{25} 0·9209, 0·9161, 0·9136; ...... a 100 mm. tube), +2·85°, +2·84°, +6·6°; n_D 1·4675, 1·4713, ...53, saponification number, 12·5, 14·40, 16·6; saponification

number after acetylation, 75·1, —, 65·7. Calculating the amount and esters as borneol and bornyl acetate, the oils contained (1) 5·04%, and 5·81% of bornyl acetate, and samples (1) and (3) contain 18·44% and 14·46% of borneol respectively. Samples (1) and (3) contain 35—36% and 69—71% of cineole. Besides borneol, bornyl acetate, cineole, the oil contained d- and l-α-pinene, salicylic acid, other esters other than bornyl acetate, and probably linalool and sesqui penes.

E. G.

Oils of the Coniferæ. II. The Leaf and the Twig and Bark Oils of White Fir. A. W. SCHORGER (J. Ind. Eng. Chem., 1914, i, 809—810. Compare this vol., i, 1134).—The leaves and twigs of white fir, Abies concolor, yield from 0·029 to 0·272% of oil having D^{15} 0·8720—0·8777, n_D^{20} 1·4786—1·4796, a_D^{20} − 20·11° to − 27·34°; acid number, 1·01—1·81; ester number, 12·52—27·34. The bark has 0·095% of oil having D^{15} 0·8702—0·8767, n_D^{15} 1·4789—1·47—, a_D^{20} − 20·15° to − 20·95°; acid number, 0·87—1·22; ester number, 6·43—6·88. The composition of the oils was found to be as follows:—

	Leaf and twig oil.	Bark.
Furfuraldehyde	trace	trace
l-α-Pinene	12	9
l-Camphene	8	—
l-β-Pinene	42	62
l-Phellandrene	15	Dipentene 12
Ester, as bornyl acetate	6·5	7·7
Free borneol	9·5	1·8
"Green oil"	3	5
Loss	4	7

W. P. S.

Oil of Black Sage. CHARLES E. BURKE and CHARLES C. SCOTT (J. Ind. Eng. Chem., 1914, 6, 804—806).—Black sage (Eriodictyon Stachyoides) from Southern California yielded 0·9% of an oil, D^{15} 0·8979, [a] 24·4°, n_D 1·4729; acid number, 2·2; ester number. The oil had the following composition: pinene, 6·0%; cineole, 36% dipentene, terpinene, etc., 25·0%; thujone, 8·0%; camphor, 20% resinous substance, 5·0%.

W. P. S.

Essential Oil of Argentine Mint (Bystropogon Mollis Kth). ADOLFO DOERING (Bol. Acad. Nac. Ciencias Cordoba, 1913, 18, 379—391).—The essential oil forms about 0·4% of the plant, does not depositing crystals of menthol at 12°, has D 0·918—0·920 and distils chiefly at 210°. As much as 2·5% of furfuraldehyde is present, and is removed by means of permanganate. Free acid amounts to about 0·7%, and phenols are present in traces. Menthol appears to be absent. The terpenes have not so far been characterised.

G. D. L.

Optical Activity of Cinnamein. L. ROSENTHALER (Chem. Zentr., 1914, ii, 36—37; from Schweiz. Apoth.-Zeit., 1914, 52, 273, 290).— The rotations of the cinnameins isolated from genuine and false balsams and from some artificial products have been measured in alcoholic and ethereal solutions. The majority of the extracts of genuine balsams had a small dextrorotation. In addition,

content was determined, as well as the saponification number
balsam and of the cinnamein which was isolated from it.

J. C. W.

Synthetic **Caoutchouc.** I. I. ANDRÉEV (*Chem. Zentr.*, 1914, ii,
326, from *Ber. St. Petersburg Polytech. Inst.*, 1913, 21, 313—368).
An apparatus is described, with diagrams, in which turpentine may
accompassed by means of an electrically heated platinum wire, and
converted into isoprene. The addition of carvene, dipentene, or
atic hydrocarbons is found to improve the yield of isoprene.

J. C. W.

The Gitalin **Question.** L. ROSENTHALER (*Chem. Zentr.*, 1914, ii,
from *Schweiz. Apoth.-Zeit.*, 1914, 52, 349–350).—The author
with Kiliani (this vol., i, 857) that gitalin is a mixture. He
separated it into a fraction which forms a hydrate and one which
not, and has isolated a crystalline substance which is physiologically
active, and seems to differ from any known constituent of digitalis.

J. C. W.

Dimethylpyrone Hydrochloride. H. N. K. RODDAM (*Oversigt.
Danske Vidensk. Selskabs. Forhandl.*, 1914, 243–262).—The
investigations which have hitherto been carried out have not made it
that whether dimethylpyrone hydrochloride acts as a true salt in
solution, or whether it is resolved into the components dimethyl-
one and hydrochloric acid. In order to decide the question, the
has determined the concentration of the chloride ion in solutions
varying strength, by measuring the potential of the electrode:
with Hg_2Cl_2, solution of dimethylpyrone hydrochloride, against
[?] calomel electrode; similar measurements were made with
solutions of hydrochloric acid. The equivalent conductivities
all the solutions were also measured, and on plotting the values of
chloride ion concentrations (abscissæ) against the equivalent
activities (ordinates) it is found that the curve for dimethylpyrone
hydrochloride lies below that for hydrochloric acid, both curves
reaching the same value for infinite dilution. The conclusion is
fore that dimethylpyrone exists as a true salt in solution; it is
lysed to some extent, the hydrolysis constant being 0·63, and the
cation constant of dimethylpyrone as base is calculated to be
10^{-4} (compare Walden, A., 1902, i, 168). T. S. P.

Solanine-*s*. VIII. Nature of the Glucosidic Condensation
Solanine-*s*; Glucosides in General. GIUSEPPE ODDO and
MELLO CESARIS (*Gazzetta*, 1914, 44, ii, 181—190. Compare this vol.,
141).—The hydrolysis of solanine-*s* from *Solanum sodomaeum* yields
anine-*s*, *d*-galactose, dextrose and *d*-aldomethylpentose:

$$C_{44}H_{70}O_{15}N_7 H_2O = 2C_{18}H_{31}ON + C_6H_{12}O_6 + C_6H_{12}O_6 + C_6H_{12}O_5,$$

molecule of water of crystallisation sufficing for the decomposition.
anine-*s* does not react with phenylhydrazine or hydroxylamine;
her, the only oxygen atom of solanidine-*s* is hydroxylic, and the
gen is present in the form of the imino-group in both compounds.

From these results, the structure of solanine-s and the matter is that water is added to it on hydrolysis are represented thus:

$$\text{NH:C}_{14}\text{H}_{20}\text{O} \quad -\text{CH·O} \quad \overset{O}{\underset{\text{CH}}{|}} \quad \text{O·CH} \quad \overset{H}{\underset{(\text{OH·H}_2)}{|}}$$

$$[\text{CH·OH}]_4 \quad [\text{CH·OH}]_4 \quad [\text{CH·OH}]_4$$

$$\text{CH}_2\text{·OH} \quad \text{CH}_3 \quad \text{CH}_2\text{·OH}$$
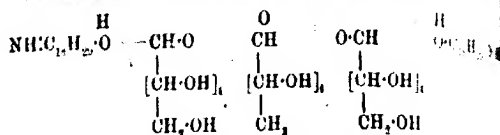
Solanidine.   Dextrose.   Methylpentose.   d-Galactose.

The results obtained by Oddo and Mameli (A., 1904, i. 2??) ??? acetals prepared from dichloroacetaldehyde hydrate are utilised elaborating a theory to explain the synthesis of solanine from constituents.   T. H.

Solanine-s. IX. Solanidine sodomaeum and Some of Products of Disintegration. GIUSEPPE ODDO AND MARCELLO (Gazzetta, 1914, 44, ii, 191—208).—Solanidine ether, (NH:?·H?) obtained by the action of hydrochloric acid on solanidine in alcoholic solution, crystallises in needles, m. p. 176—177°, $[\alpha]_D$ −141·5 in benzene and has the molecular weight 373—425 in freezing benzene, 248—259 in freezing acetic acid, the calculated value being ??. When its alcoholic solution is poured on to concentrated ??? acid, a yellow ring, changing to orange, forms at the surface separation. When treated with nitrous acid, the ether yields a compound, $[\text{N(OH)}_2\text{·C}_{18}\text{H}_{29}\text{N·O·C}_{18}\text{H}_{29}\text{N}]_2\text{N·OH}$, 2 mols. of ether reacting with 3 mols. of the acid, with elimination of H. This compound forms pale reddish-yellow needles, m. p. 224—? (decomp.). It gives neither a blue coloration with diphenylamine the characteristic reaction of nitroso-compounds with Liebermann reagent. When treated with acid or alkali, it yield solanidine ether.

The compound described as azosolanidine (A., 1911, i, 671) is found have the composition $\text{C}_{72}\text{H}_{116}\text{O}_9\text{N}_8[=4(\text{C}_{18}\text{H}_{31}\text{ON,HNO}_2)-3\text{H}_2\text{O}]$. When treated with hydrochloric acid it gives dihydrosolanidine $\text{C}_{18}\text{H}_{33}\text{Cl}$ (?), m. p. 113°, and another compound, m. p. ??? which appears to be a chlorinated alcohol, $\text{C}_{18}\text{H}_{23}\text{OCl}$.

No definite compounds could be separated from the products action of energetic dehydrating or oxidising agents on solanidine.
                                                                T. H.

Action of Nitrous Acid on Amines. Behaviour Towards Tropigenine and Granatoline. I. GIUSEPPE ODDO and MARIO CESARIS (Gazzetta, 1914, 44, ii, 209—227).—From the results of investigations on the action of nitrous acid on solanine-s and solanidine (compare preceding abstract), the authors draw the conclusion that action of nitrous acid on a primary or secondary amine results in formation of the corresponding nitrite, $\text{NHR}^1\text{R}^2\text{,HNO}_2$, which undergoes transformation into an as-dihydroxyhydrazine derivative $\text{NR}^1\text{R}^2\text{·N(OH)}_2$. The further decomposition of the latter varies the nature of the radicles present, and may follow one or other of three types, which have been named: (1) Anazoic. In this ammonium nitrite yields nitrogen and water; primary amines, the

and an alcohol, and secondary amines, nitrogen and either alcohols, or, if $R^1 = R^2$, a single alcohol. (2) *Diazoic.* Here, ammonium nitrite yields nitrosoamine, $NH_4 \cdot NO$, or *iso*nitrosoimide, $NNOH$, primary amines give nitrosoamines, $NHR \cdot NO$, or diazohydrate, $R \cdot N:N \cdot OH$, and secondary amines, true nitroso-compounds, $R_2 N \cdot NO$. (3) *Cyclazoic,* which either gives stable azocyclic compounds or ψ-nitroso-compounds, such as $\begin{matrix} C_8H_{14} \\ CO \end{matrix} > C < \begin{matrix} N \cdot OH \\ NH \end{matrix}$, from camphor nitrite, or results in the opening of the nucleus and formation of *allo*nitroso-compounds, for instance, *allo*nitroso-oxindole $C_6H_4 < \begin{matrix} CH(NO) \\ NH \end{matrix} > CO$, from ψ-nitroso-oxindole,

$$C_6H_4 < \begin{matrix} CH \\ CO \\ N \end{matrix} > N \cdot OH.$$
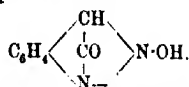
A true dihydroxyhydrazine derivative is obtained by the action of this acid on the ether of solanidine-*s* (*loc. cit.*). With the compound obtained from solanine-*s* and solanidine-*s*, the complete elimination of the nitrogen by the action of acids shows that in these cases the action of nitrous acid proceeds immediately to the cyclazoic stage. Since the sole difference between solanidine-*s* and its ether consists in the presence of a hydroxyl group in the former, it has been thought desirable to study the action of nitrous acid on tropigenine and granatoline, which are saturated, alicyclic, iminic, alcoholic bases of similar structure. In aqueous solution faintly acidified with acetic acid tropigenine yields the corresponding nitrite at the ordinary temperature. At the temperature of a boiling-water bath, however, the reaction yields a compound which has the composition, but none of the properties of the true nitroso-compound (I) and is regarded as the cyclic ψ-nitroso-compound (II):

$$\begin{matrix} CH_2 \cdot CH - CH_2 \\ | \quad N \cdot NO \quad CH \cdot OH \\ CH_2 \cdot CH - CH_2 \\ (I.) \end{matrix} \qquad \begin{matrix} CH_2 \cdot CH - CH_2 \\ | \quad N \cdot N(OH) \cdot O \cdot CH. \\ CH_2 \cdot CH - CH_2 \\ (II.) \end{matrix}$$
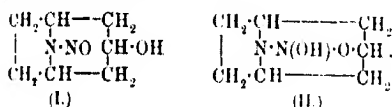
This compound is accompanied by two others in small proportions, the more abundant having the properties of the hydrate of a true nitroso-compound, that is, of the intermediate dihydroxyhydrazine derivative. The interaction of granatoline hydrochloride and silver nitrite gives nitrite of the base, and this in aqueous solution is converted by this acid into the hydrate of the true nitroso-compound (III) (compare Ciamician and Silber, A., 1895, i, 160).

$$\begin{matrix} CH_2 \cdot CH - CH_2 \\ CH_2 \, N \cdot N(OH)_2 \, CH \cdot OH \\ CH_2 \cdot CH - CH_2 \\ (III.) \end{matrix} \qquad \begin{matrix} CH_2 \cdot CH - CH_2 \\ CH_2 \, N \cdot N(OH) \cdot O \cdot CH \\ CH_2 \cdot CH - CH_2 \\ (IV.) \end{matrix}$$
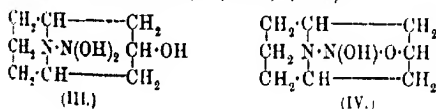
In vacuum, this hydrate gradually loses $1 H_2O$, with formation of the

compound, m. p. 125°, which was obtained by Ciamician and ???
and is the ψ-nitroso-compound (IV).

Tropigenine nitrite, $C_7H_{13}ON,HNO_2$, prepared by the action
silver nitrite on the hydrochloride of the base, forms a ???
crystalline powder, which turns yellow at about 100° and ???
m. p. 160°.

ψ-*Nitrosotropigenine* (formula II) forms rosettes of white ???
m. p. 195—196°. *Nitrosotropigenine hydrate* has a structure ana???
to that of the corresponding granatoline derivative (formula II???
forms white crystals, m. p. about 160° (decomp.).

Granatoline nitrite, $C_{19}H_{15}ON,HNO_2$, forms white needles, m.
215—216° (decomp.). Nitrosogranatoline hydrate (formula II???
white leaflets, m. p. 72—73°. ψ-Nitroso-granatoline (formula II
m. p. 125°, yields an *ethyl ether*, $C_{10}H_{13}O_2N_2$, white prisms, m.
65—67°.   T. H. P.

Direct Attempts to Prepare Ferropyrroles. I. B???
ODDO (*Gazzetta*, 1914, **44**, ii, 268—278).—The author discusses ???
occurrence of iron and magnesium in hæmoglobin and chloro???
respectively and their derivatives. It is not found possible to prep???
organic ferro-compounds containing alkyl or aryl groups, the action
ferric chloride on magnesium ethyl bromide being a chloridi???
action, expressed by the equation :

$$MgEtBr + Fe_2Cl_6 = EtCl + 2FeCl_2 + MgBrCl.$$
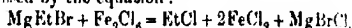
With magnesium phenyl bromide and magnesium benzyl bromide ???
action of ferric chloride yields diphenyl and dibenzyl respectively ???
result indicating the intermediate formation of an organo-iron com???
which then undergoes decomposition, thus :

$$2FePh_2Cl = C_6H_5Ph + FeCl_2 + Fe.$$
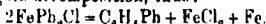
With an organo-magnesium derivative containing a 2-methylindyl
residue, the action of ferric chloride gives, however, a non-metal
di-2-methylindolyl ferrichloride, $CH{<}_{CMe}^{C_6H_4}{>}N\cdot FeCl\cdot N{<}_{CMe}^{C_6H_4}{>}$???
yellow solid, blackening and contracting at about 130°, and remain
unmelted at 230°.   T. H. P.

Salts of Acridine, Pyridine, and Quinoline. II. L. H. ???
(*J. Amer. Chem. Soc.*, 1914, **36**, 2101—2110).—It has been shown ???
the author (A., 1913, i, 92) that when diphenylacridyl chloride
5-phenyl-10-methylacridyl chloride is shaken with nitrobenzene ???
molecular silver, a highly coloured solution is produced when ???
oxygen. It was assumed that these coloured solutions contain ???
acridyl radicles analogous to triphenylmethyl. Evidence has now ???
obtained which proves the accuracy of this assumption, and new
unsaturated acridyl radicles and their peroxides have been isol???
The free radicles are dark brownish-red, crystalline substances wh???
in solution absorb oxygen from the air to form colourless perox???
and also unite directly with halogens with production of ???
corresponding haloids. They are best prepared by shaking an aqu???
solution of a salt, preferably the sulphate, with zinc dust. The ???

coated with the free radicle and the liquid becomes colourless. Decanting the colourless solution and adding benzene to the moist for, the benzene dissolves the free radicle, forming a dark red lax. On shaking this benzene solution with air, its colour rapidly years and the colourless peroxide soon begins to separate.

Diphenylacridyl, $C_{25}H_{18}N$, can be prepared by the method already noted or less satisfactorily by the electrolysis of its normal sulphate; fuses when heated and melts at about 185—190°. Molecular weight ruminations have shown that it exists mainly in the unimolecular state. The radicle unites instantly with chlorine to form yellow *diphenylacridyl chloride*, and also dissolves slowly in hydrochloric acid production of the chloride. The *peroxide*, $C_{50}H_{36}N_2O_2$, crystallises under, pale yellow prisms, and when heated begins to darken at 190° and melts at 204—207° according to the rate of heating; it runs slowly in mineral acids with formation of the corresponding salts. When an aqueous solution of diphenylacridyl chloride noted with zinc dust, diphenylacridyl is produced together with a quantity of *dihydrodiphenylacridine* ("*diphenylacridane*"), N, m. p. 175°, which crystallises in cubes; this substance can be prepared by adding zinc dust to a boiling solution of diphenyl- in acetic acid.

following substances have also been prepared together with salts, free radicles, and peroxides, and will be described sently: *p*-chlorophenyl-10-phenylacridol, *p*-methoxyphenyl-10-acridol, 2:4-dimethoxyphenyl-10-phenylacridol, phenyl-10-methyl- and phenyl-10-ethylacridol.   E. G.

XV. 5-Amino-6-ethylamino-2:3-dihydro-2-pyridone and 2:8-Dioxy-9-ethyl-2:3:8:9-tetrahydro- CARL O. JOHNS and BYRON M. HENDRIX (*J. Biol. Chem.*, 1914, 5-50. Compare this vol., i, 440).—2:8-Dioxy-9-ethyl-2:3:8:9- hydropurine has been prepared for the purpose of comparing properties with those of the methylated compounds, 2:8-dioxy-6-methyl-2:3:8:9-tetrahydropurine (A., 1913, i, 1000) and 2-methyl-9-ethyl-2:3-dihydropurine (*ibid.*, i, 1397).

Ethylthiol-6-ethylaminopyrimidine, $NHEt \cdot C \underset{CH=CH}{\overset{N \cdot C(SEt)}{<}} N$, b. p.

11 mm., obtained in almost quantitative yield by heating 2-ethylthiolpyrimidine and 33% aqueous ethylamine at in a sealed tube, is converted by boiling with concentrated hydrochloric acid and subsequent evaporation to dryness with hydroxide into 6-*ethylamino*-2:3-*dihydro*-2-*pyrimidone*, N, bluntly pointed prisms, m. p. 218°. The latter, by with concentrated sulphuric acid and nitric acid (D 1·5) 70°, yields quantitatively 5-*nitro*-6-*ethylamino*-2:3-*dihydro*-2-dione, acicular prisms, decomp. 275°, which is converted into 5-6 *ethylamino*-2:3-*dihydro*-2-*pyrimidone*, stout prisms, decomp. by reduction with aqueous ammonia and ferrous sulphate at the ny temperature. The base develops in ammoniacal solution a blue coloration with phosphotungstic acid and reacts with red carbamide at 170—180° to form 2:8-*lioxy*-9-*ethyl*-2:3:8:9-

tetrahydropurine, $\overset{N=CH\cdot C\cdot NH}{\underset{CO\cdot NH\cdot C\cdot NEt}{\big|}}$ $>$ CO, small prisms, decomp. at 300°.

Etherification of *o*-Hydroxyazo-compounds. V. G. CRUM and G. FERRARI (*Gazzetta*, 1914, **44**, ii, 228—256. Compare this i, 597, 599, 748).—The *o*-hydroxyazo-compounds derived from a-naphthol and from 10-hydroxyphenanthrene, that is, the 2-arylazo-naphthols and the 9-arylazo-10-hydroxyphenanthrene, react with methyl or ethyl sulphate in the presence of concentrated alkali solution, thus :

$$OH\cdot C_{10}H_6\cdot N:NAr + SO_2(OR)_2 + KOH =$$
$$OR\cdot C_{10}H_6\cdot N:NAr + OK\cdot SO_2OR + \text{...}$$
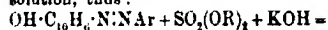
The ethers obtained in this way are well-crystallised, orange or red compounds, which are markedly more soluble in organic solvents, and melt, without decomposing, at lower temperatures than the corresponding *o*-hydroxyazo-compounds. They are also decidedly basic than the latter, owing to the intensification of basic properties of the oxygen consequent on etherification. All salts isolated and analysed contain two equivalents of acid, and of the 10-hydroxyphenanthrene series, which could not be isolated react as though the base is diacid. To these salts, therefore, attributed one of the two tautomeric structures :

$$X\cdot OHR\cdot C_{10}H_6(\text{or } C_{14}H_8)\cdot N:NHXAr \text{ or}$$
$$X\cdot OR\cdot C_{10}H_6(\text{or } C_{14}H_8):N:NHXAr$$
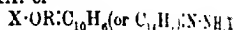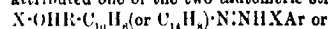
where X represents a halogen atom or a univalent acid residue. Nascent hydrogen decomposes the ethers into a primary amine NH, and an ether of an aminophenol, $OR\cdot C_{10}H_6(\text{or } C_{14}H_8)\cdot NH_2$. The ethers are extremely resistant to the action of boiling concentrated alkali hydroxide solution, but towards acids their behaviour is varied. The 2-arylazo-1-naphthols are, with some exceptions, highly resistant to boiling dilute or concentrated acid, and, when heated, their acid chlorides suffer loss of hydrogen chloride without decomposition of the ether ; on the other hand, the 9-arylazo-10-hydroxyphenanthrene and also 2-*o*-methoxy- and 2-*o*-ethoxy-benzeneazo-1-naphthols are hydrolysed readily by dilute acid, their hydrochlorides being largely decomposed on heating into the corresponding hydroxyazo-compounds and chlorides of the alkyl radicles of the ethers.

2-*Benzeneazo*-1-*naphthyl methyl ether hydrochloride,* $C_{17}H_{14}ON_2Cl$ forms dark red needles with metallic, green reflection ... Noelting, Grandmougin, and Freimann, A., 1909, i, 442).

2-Benzeneazo-1-naphthyl ethyl ether has m. p. 46° ; Noelting, Grandmougin, and Freimann (*loc. cit.*) gave 44°. Its *hydrochloride,*
$$C_{18}H_{16}ON_2, 2HCl,$$
forms dark garnet-red scales with metallic, golden reflection ; *nitrate,* $C_{18}H_{16}ON_2, 2HNO_3$, loses nitrous vapours at 47—49°, residue melting at 143—145°.
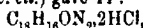
2-*o*-*Tolueneazo*-1-*naphthyl methyl ether,* $OMe\cdot C_{10}H_6\cdot N:N\cdot C_6H_4$, crystallises in mammillary masses of orange-yellow needles, m. p. 60—61°, and forms a red solution in concentrated sulphuric acid ; its *hydrochloride* forms shining, cantharides-green scales. The d...

... methyl ether, $C_{19}H_{18}ON_2$, forms yellow, acicular crystals, m. p. ... hydrochloride, metallic golden scales).

m-Toluenezzo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4Me$, prepared by the action of m-tolylhydrazine hydrochloride on β-naphthaquinone, forms axillary aggregates of slender, bright red needles, m. p. 117—118°, yields a ruby-red solution in concentrated sulphuric acid. The methyl ether forms chrome-yellow scales, m. p. 49—50°, and its hydrochloride bronze needles. The ethyl ether forms orange-red prisms, m. p. 33°, and its hydrochloride, mammillary masses of garnet-red ...

p-Toluenezzo-1-naphthyl methyl ether forms orange-red needles, m. p. 77—78°, and its hydrochloride, minute, brick-red needles. The ethyl ether forms slender, orange-yellow needles, m. p. 51°, and its hydrochloride, deep garnet needles.

as-m-Xylenezzo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_3Me_2$, prepared by action of as-m-xylylhydrazine hydrochloride on β-naphthaquinone, as deep red scales or needles with metallic, golden reflection, m. p. ... The methyl ether forms slender, orange-yellow crystals, m. p. ... and its hydrochloride, metallic, green crystals. The ethyl ether is bright red prisms, m. p. 89°, and its hydrochloride, golden scales.

s, Cumenezzo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_2Me_3$, crystallises in leaflets or needles with faint golden reflection, m. p. 194—195°. The methyl ether forms orange-yellow prismatic needles, m. p. 82—83°, its hydrochloride, golden-green leaflets. The ethyl ether forms red ..., m. p. 64°, and its hydrochloride, cantharides-green needles.

p-Chlorobenzenezzo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4Cl$, forms bright ruby needles, m. p. 187°. The methyl ether crystallises in orange leaflets, m. p. 111°, and its hydrochloride in dark green, the needles. The ethyl ether forms orange-red, acicular crystals, m. p. 84—85°, and its hydrochloride, heavy, cantharides-green plates.

Methoxybenzenezzo-1-naphthyl methyl ether,

$$OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OMe,$$
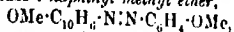
bright red prisms, m. p. 90—91°, and its hydrochloride, greenish-green needles or leaflets with metallic reflection. The ethyl ether forms red prisms, m. p. 88—89°, and its hydrochloride, slender, cantharides-green needles.

Ethoxybenzenezzo-1-naphthyl methyl ether,

$$OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OEt,$$
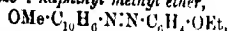
arises in brick-red needles, m. p. 62°, and its hydrochloride, in cantharides-green needles. The ethyl ether forms bright red needles, 62°, and its hydrochloride, slender, bronze-green needles.

Benzenezzo-10-methoxyphenanthrene, $OMe \cdot C_{14}H_8 \cdot N:NPh$, forms bright red prisms, m. p. 88—89°, and, on reduction by means of dust and acetic acid, yields aniline and a basic compound, which is only 9-amino-10-methoxyphenanthrene. The corresponding 10-hydro derivative, $C_{22}H_{18}ON_2$, forms bright red, flattened needles, m. p. ... and on treatment with ethereal nitric acid yields benzene-diazonium nitrate, 9-nitro-10-ethoxyphenanthrene, and a compound crystallises in pale red needles, m. p. 249—250° (decomp.), and is bly a nitro-9-benzenezzo-10-hydroxyphenanthrene; its behaviour daction appears similar to that of the methoxy-compound.

The interaction of *as.*-phenylmethylhydrazine hydrochloride and phenanthraquinone in boiling acetic acid yields neither benzene-izo-10-hydroxyphenanthrene nor its methyl ether, compound which forms pale yellow leaflets, m. p. 221—222° and under investigation.

9-o-*Tolueneazo*-10-*hydroxyphenanthrene*, $OH \cdot C_{14}H_8 \cdot N \colon N \cdot C_6H_4$, forms minute, orange-red scales with golden reflection, m. p. 232—, and the corresponding *ethyl ether*, flat, garnet-coloured tablets, m. p. 109°.

9-p-*Tolueneazo*-10-*hydroxyphenanthrene*, $C_{21}H_{16}ON_2$, forms bright red needles, m. p. 169°; its *methyl ether*, dense, bright needles, m. p. 117°, and its *ethyl ether*, lustrous, bright red, m.p. 158°.

9-o-*Methoxybenzeneazo*-10-*hydroxyphenanthrene*,

$$OH \cdot C_{14}H_8 \cdot N \colon N \cdot C_6H_4 \cdot OMe,$$

forms red leaflets with golden reflection, m. p 245—247, and *ethyl ether*, red needles, m. p. 140—141°.   T H ?

Aminoazo-compounds. L. CASALE and MARIA CASALE SENA (*Atti R. Accad. Sci. Torino*, 1914, **49**, 1199—1203).—The authors have prepared a number of new aminoazo-compounds by coupling a-naphthylamine with diazonium salts obtained from amines substituted in the ortho-position. In the products obtained, which form well crystallised and moderately stable salts with acids, the azo-group occurs in the para-position to the amino-group of the naphthalene residue, since 4-o-tolueneazo-1-naphthylamine, for example, yields naphthylene-1 : 4-diamine on reduction.

4-o-*Tolueneazo*-1-*naphthylamine*, $C_6H_4Me \cdot N \colon N \cdot C_{10}H_6 \cdot NH_2$, crystallises in bright red, silky needles, m. p. 95°, and yields those solutions in chloroform, benzene or alcohol, and an intensely red solution in acetic acid; it gives a red coloration with concentrated and a violet one with dilute, sulphuric acid. Its *monoacetyl* derivative, $C_6H_4Me \cdot N \colon N \cdot C_{10}H_6 \cdot NHAc$, orange-red needles, m. p. 215—216, a derivative, $C_6H_4Me \cdot N \colon N \cdot C_{10}H_6 \cdot NAc_2$, brick-red, prismatic, m. p. 136°, and *benzoyl* derivative, $C_6H_4Me \cdot N \colon N \cdot C_{10}H_6 \cdot NHBz$, yellow needles, m.- p. 200°, were prepared. When excess of sodium nitrite is used in the diazotisation of the o-toluidine, the above compound is accompanied by 4-o-tolueneazo-1-naphthol.

4-o-*Methoxybenzeneazo*-1-*naphthylamine*, $OMe \cdot C_6H_4 \cdot N \colon N \cdot C_{10}H_6 \cdot N$, forms tufts of crimson needles, m. p. 184—185°, and gives deep solutions in chloroform, alcohol or ether, and an intensely violet in acetic acid. Its *acetyl* derivative, $OMe \cdot C_6H_4 \cdot N \colon N \cdot C_{10}H_6 \cdot NH$, forms garnet-red needles, m. p. 203—204°, and its *benzoyl* derivative $C_{24}H_{19}O_2N_3$, orange-red needles, m. p. 182°. Here, too, the use sodium nitrite in excess results in the formation of 4-o-methoxy-benzeneazo-1-naphthol (compare Charrier and Casale, this vol., 748).

4-o-*Ethoxybenzeneazo*-1-*naphthylamine*, $OEt \cdot C_6H_4 \cdot N \colon N \cdot C_{10}H_6 \cdot N$, forms groups of vermilion crystals, m. p. 169°; its *acetyl* derivative $C_{20}H_{19}O_2N_3$, red, prismatic needles, m. p. 191°, and its *benzoyl* derivative $C_{25}H_{21}O_2N_3$, tufts of green, silky needles, m. p. 180°.

p-Nitrobenzeneazo-1-naphthylamine, $NO_2 \cdot C_6H_4 \cdot N\!:\!N \cdot C_{10}H_6 \cdot NH_2$, shining, emerald-green scales, m. p. 174—175°, and gives nearly red solutions in alcohol, benzene, chloroform or ether. Its *acetyl* derivative, $C_{18}H_{14}O_3N_4$, forms tufts of shining, pale green needles, p. 200°, and its *benzoyl* derivative, $C_{23}H_{16}O_3N_4$, shining, black with red reflection, m. p. 185°.

T. H. P.

Phosphorus Content of Caseinogen. ALFRED W. BOSWORTH and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1914, **19**, 67—71. Compare A., 1913, i, 659).—Additional evidence is adduced to show that caseinogen contains only about 0·7% of phosphorus (compare Rice and Macallum, this vol., i, 442).

H. W. B.

Mode of Action of Urease and of Enzymes in General. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1914, **19**, 141—180. Compare this vol., i, 606).—The consideration of the work already published (*loc. cit.*), and now described in detail, leads to the conclusion that urease destroys urea by means of two successive stages: (1) combination of enzyme and substrate; (2) disruption of the combination, the urea being freed as ammonia and carbon dioxide. This process is formulated in accordance with the law of mass action, and the equation $t = 1/E[1/c \log a/(a-x) + x/d]$, where a represents the amount of substrate (urea) present per unit volume at the beginning of the reaction, x the amount decomposed in time t, c the enzyme concentration, c the velocity of combination of enzyme and substrate, and d the velocity at which the combination decomposes, giving ammonium carbonate and free enzyme, is found accurately to express all the results thus far obtained.

H. W. B.

Effect of Hydrogen Ion Concentration and of Inhibiting Substances on Urease. DONALD D. VAN SLYKE and GOTTHARD MARIAS (*J. Biol. Chem.*, 1914, **19**, 181—210. Compare Marshall, this vol., 606; Armstrong and Horton, A., 1912, i, 594; and the preceding abstract).—The authors have measured the rates of decomposition of urea by urease when the hydrogen ion concentration has been kept at constant levels by Sörensen's method (A., 1909, i, 861). Changes in the concentration of hydrogen ion have absolutely direct and independent effects on the two successive reactions (i) combination with substrate; (ii) decomposition of combined substance, by which the enzyme destroys urea. Throughout the range of experimental observation ($P_H = 5·9$ to 8·7), the combining velocity has been found to vary in inverse ratio to the hydrogen ion concentration (the more alkaline the solution the more rapid the combination), but the decomposition by enzyme of the urea combined with it is most rapid in neutral solution and is retarded by either alkalinity or acidity.

In the absence of inhibiting substances such as salts and dextrose, provided the concentration of urea lies between 0·08 and 10%, combination of urease and urea is so quick that it consumes a hardly measurable proportion of the total time, which is almost entirely taken up by the slower decomposition reaction. The maximum rate of

ammonia formation under these conditions is consequently that of the decomposition reaction, and takes place when the solution is maintained at the neutral point. When, however, the reaction is retarded by adding neutral salts or using dilute solutions, it becomes an appreciable factor in the total time reaction, and the optimum hydrogen ion concentration for the enzyme action is therefore shifted towards the alkaline side effect of hydrogen ion concentration on invertase may also be accounted for as the sum of independent effects on the two separate phases of enzyme action.

The effect of the generated ammonium carbonate in retarding the action of urease is due chiefly to the alkalinity of the carbonate. When a phosphate mixture prevents the ammonium carbonate from affecting the hydrogen-ion concentration, it also prevents its effect on the velocity. Neutral salts retard the action of urease by interfering with the combination of enzyme with substrate. This effect is the greater the more dilute the urea solution, and consequently it is especially the decomposition of the last traces of urea that is retarded by neutral salts.

Dextrose retards the enzyme action in the same manner as neutral salts. Alcohol in 30% concentration depresses both phases of the enzyme's action. Both electrolytes and non-electrolytes in more than bimolecular concentration retard the enzyme action in its second phase, namely, the decomposition of urea after it has combined with urease. All these effects can be represented by the general mass action formula for enzyme action already set forth (*loc. cit.*).　　　H. W. B.

Enzyme Action. XI. **Some Experiments** with Castor bean Urease. K. GEORGE FALK and K. SUGIURA (*J. Amer. Chem. Soc.*, 1914, **36**, 2166—2170).—In an earlier paper (Falk, A. 1913, i) it has been shown that castor beans contain a urease. Further experiments have now been made in comparison with the urease of soja beans. It has been found that, under comparable conditions, soja bean preparations hydrolyse much less urea than similar castor bean preparations. The action of acids, bases, and salts on the hydrolysis of urea by castor bean urease has been studied and results have been found similar to those which have been observed in the case of soja bean urease.　　　E. G.

Physiological Chemistry.

Influence of Pituitrin on Respiration. L. B. NICE, J. L. and R. O. COURTRIGHT (*Amer. J. Physiol.*, 1914, **35**, 144—15). The characteristic effect of pituitary extract on respiration is increase in the depth, followed by a shallowness and a decrease in the rate of breathing. In some cases, however, the increase in

...th of respiration is followed by shallowness and an increase
the rate of breathing. The effect of pituitrin on the respira-
tory mechanism occurs synchronously with that on the circulatory
system. The effect on respiration, however, passes off sooner than
that on circulation. After a few injections of pituitrin, the
respiratory mechanism becomes immune and the characteristic
pauses are not elicited.   H. W. B.

Normal Level of Blood-Sugar of the Dog. PHILIP A.
SHAFFER (*J. Biol. Chem.*, 1914, **19**, 297—302).—The author finds
that the concentration of dextrose in the blood of normal dogs,
when the animals are free from excitement or pain, is in the neigh-
bourhood of 0·05%, or about one-half to one-third the values
usually accepted as normal. Higher figures are obtained after
exertion or when the animal is excited. These higher results
are comparable with those hitherto regarded as normal, which
may represent varying degrees of emotional hyperglycæmia
brought about by the procedure of drawing the blood.
                                                                   H. W. B.

**The Fat of Blood. I. Fat Content of the Blood under
approximately Normal Conditions.** W. R. BLOOR (*J. Biol.
Chem.*, 1914, **19**, 1—24).—The author has determined the fat content
of the blood, in various circumstances, by his nephelometric
method (this vol., ii, 392). In normal circumstances, the fat con-
tent of the blood is practically constant, both for the individual
and the species, amounting to 0·59 gram per 100 grams of blood.
After a fat meal, the fat in the blood increases gradually, reach-
ing a maximum in about six hours. If the thoracic duct is tied,
however, an increase in the fat does not occur after feeding with
fat. Intravenously injected fat, in quantities up to 0·4 gram
per kilo. of body-weight, disappears from the blood within five
minutes. When larger amounts are injected, some of the fat
remains in the blood for several hours. Apparently the liver is
able to withdraw from the blood, and loosely store, a certain
amount of fat, but the storage capacity is limited.

Ether and the administration of chloroform produce an in-
crease in the fat of blood only when the animal has previously
been well supplied with fatty foods. Ether, however, regularly
causes a rise in the fat content of the blood during the narcosis.
The loosely stored fat may, therefore, be quickly released by certain
drugs, and the sudden flooding of the organism with fat may be
an actual source of danger. In the animals that died under the
ether there was observed a rapid and continuous rise in the
fat content of the blood during the anæsthesia until death.
                                                                   H. W. B.

**Urea and Total Non-Protein Nitrogen in Normal Human
Blood: Relation of their Concentration to Rate of Elimin-
ation.** FRANKLIN C. McLEAN and LAURENCE SELLING (*J. Biol. Chem.*,
1914, **19**, 31—38).—The authors have determined by Folin's methods

the relation between the concentration of urea in the b...
its corresponding rate of elimination in the urine. The con...
tion of urea and of total non-protein nitrogen in norma...
blood varies within wide limits according to various fac...
as diet, amount of fluid ingested, etc. There is, however,...
parallelism between the concentration of urea in the ...
the amount excreted in the urine in normal indivi...
average conditions. The elimination of urea is retard...
sufficient water is taken, and the retention of urea is ev...
marked in cases of nephritis. A high concentration of ...
the blood is not necessarily a sign of pathological renal ...
unless associated with a relative decrease in the amount ...
eliminated in the urine.
H. W.

Proteins of the Blood of Limulus Polyphemus. L. ...
ALSBERG (*J. Biol. Chem.*, 1914, **19**, 77--82).—The proteins of ...
blood of *Limulus* consist almost exclusively of the clo...
(which differs greatly from ordinary fibrinogen) and hæm...
Hæmocyanin is several times as abundant as the clo...
Other proteins occur only in minimal amounts. The bloo...
contains a small amount of nitrogen in non-coagulable ...

The quantity of protein in the blood seems to vary ...
state of nutrition of the animal, diminishing in star...
blood of *Octopus* contains at least twice as much hæm...
that of *Limulus*. The hæmocyanin of *Limulus* con...
67 68 %.
H. W.

**Carbohydrate Metabolism. VII. Influence of Subcuta...
Injections of Dextrose and of Calcium Lactate on ...
Sugar in the Blood and on Tetany after Thyr...
thyroldectomy.** FRANK P. UNDERHILL and NORMAN R. Blatter...
(*J. Biol. Chem.*, 1914, **19**, 119--126). Compare this vol. ...
The hypoglycæmia resulting from thyreoparathyroidecto...
to be neither the cause nor the effect of the accompany...
for although injections of dextrose raise the sugar ...
to the normal amount, such injections have little infl...
tetany. Moreover, the condition of hypoglycæmia pre...
of tetany. The authors therefore suggest that the remo...
thyroids and parathyroids gives rise to two distinct e...
affecting the mechanism concerned in the maintenance ...
content of the blood at its normal level, thereby caus...
glycæmia, and the other acting on the nervous system, pro...
tetany. Calcium appears to be intimately associated with ...
effects, for injections of calcium lactate will temporarily r...
normal sugar content of the blood and also abolish teta...
H. W.

Basal Metabolism and Creatinine Elimination. WALTE...
PALMER, JAMES H. MEANS, and JAMES L. GAMBLE (*J. Biol.*...
1914, **19**, 239--241).—The authors have determined the rela...
ship between basal metabolism (minimum heat producti...

...dual at rest, at least twelve hours after food, and surrounded ...temperature of 30°) and the total mass of active protoplasm ...metabolism of which is represented by the urinary creatinine ...ated on a creatine–creatinine-free diet. The number of ...us per mg. of creatinine varied in eight men from 0·89 to ...average 0·98, whilst in nine women the number ranged from ...to 1·37, average 1·26. Definite conclusions as to the value ...significance of these results are deferred until further observa- ...have been made.　　　　　　　　　　　　　　　　　H. W. B.

...eous **Exchange in Decerebrate Animals.** CHARLES G. L. ...y and T. S. HELE (*J. Physiol.*, 1914, 48, 428—442). The ...cerebrate animal responds to carbohydrates and proteins in the ...e way as the intact animal. The rise in the total metabolism ...wing administration of protein is accompanied by a rise in ...non-protein nitrogen of the blood. The decerebrate animal ...ponds to small amounts of amino-acids, such as glycine, which ...a very considerable rise in the protein metabolism. Glycine ...injected into the blood-stream, causes a greater rise in meta- ...m than was found by Lusk (A., 1913, i, 123), who adminis- ...d this substance *per os.*　　　　　　　　　　　　　　S. B. S.

...hibition of **Autolysis [of Liver] by Alcohol.** H. GIDEON ...ls and GEORGE T. CALDWELL (*J. Biol. Chem.*, 1914, 19, 57—65).— ...se experiments were performed primarily to ascertain what ...ngth of alcohol is necessary to preserve specimens of tissue ...ed for histological purposes. The results show that for the ...plete suppression of autolytic disintegration of liver tissue by ...ld, the actual strength of alcohol present cannot be safely ...than 90%; between 80 and 90% a slight autolysis may take ...ce and below 80% alcohol concentration, autolysis is certain to ...place at either room or incubator temperature. Small blocks ...tissue not greater than 5 × 1 × 1 cm. must therefore be placed ...ctly in at least 50 c.c. of 96% alcohol to prevent autolytic ...ges.

...hen experimenting with finely minced tissues, at least 10 c.c. ...better, 15 c.c., of 96% alcohol must be added for each gram of ...ue to ensure effective preservation. When not contra- ...cated, it is best to boil the tissues a short time in the alcohol ...estroy the enzymes.　　　　　　　　　　　　　　　H. W. B

...tabolic **Changes in Muscular Tissue. I. The Fate of ...njected Amino-acids.** S. A. MATTHEWS and C. FERDINAND ...ss (*J. Biol. Chem.*, 1914, 19, 229—234. Compare Fiske and ...ner, this vol., i, 1019).—After repeated injections of a diuretic ...solution into (1) dogs with an Eck-fistula, and (2) eviscerated ...s the urine becomes practically free from ammonia, and con- ...ains a small amount of nitrogenous substances. If, now, a ...tion of mixed amino-acids is injected subcutaneously, ammonia ...ars in the urine, followed usually by an increase in the amount ...rea. The conclusion drawn by the authors is that the first

action of the tissues on amino-acids is the formation of ....
and then the production of urea. The latter chang.. .. ..
to be capable of being brought about by the tissu.. ... ...
assistance of the liver.   H W ..

Reversibility of the Geotropism of Arenicola ....
Salts. SAKYO KANDA (*Amer. J. Physiol.*, 1914, 35, 16...
The addition of calcium and magnesium salts in iso......
to sea-water containing the larvæ of *Arenicola* ......
the normal negative geotropism of these organisms with....
ing the normal positive heliotropism.   Sodium a.. ....
salts, as well as acids and alkalis, have no action on th.. ....
geotropism, but prevent the appearance of positive he......
The reversal of the negative geotropism of the larv.. ....
osmotic effect, but is due to the specific action of the ca....
magnesium ions.   H W ..

Purine Enzymes of the Opossum (Didelphis Virg.....
GEORGE T. CALDWELL and H. GIDEON WELLS (*J. Biol.* ....
19, 279—283. Compare Hunter and Givens, A., 1913, ...
the tissues of the opossum, enzymes acting on free purin.. ..
were found distributed as follows: uricase (uric......
present only in the liver; xantho-oxydase, present in th.. ....
probably in the kidney; guanase, present in all tissu.. ....
probably not present in any of the tissues, except p....
liver.   H W ..

Excretion of Creatinine by Normal Women. MARTHA ..
and ELIZABETH F. CLARK (*J. Biol. Chem.*, 1914, 19, 115 ..
The analysis of the urines of twenty-six women stu.....
creatine- and creatinine-free diet gave the following aver......
for daily urinary creatinine: absolute amount elim......
gram, varying from 1·71 to 0·53; gram per kilo. of body w....
0·015, varying from 0·023 to 0·010; creatinine coefficie.. ..
creatinine nitrogen per kilo. of body-weight), 5·8, vary.. ..
9·8 to 3·5.   These figures are considerably smaller than th.. ..
sponding figures for normal men.   H W ..

Some Observations on the Excretion of Creatin..
Women. MARY HULL (*J. Amer. Chem. Sos.*, 1914, 36, 21.. ..
—The urine of several women in normal health has been sta..
The creatinine output was the chief factor considered ..
nitrogen excretion in other forms was also determined, ..
results are tabulated.   The creatinine varied between .. ..
14·97 mg. daily per kilo. of body-weight, the lowest valu.. ..
obtained in the case of a corpulent woman who lack.. ..
physical exercise.   These figures are very much lower tha..
corresponding values found for men by Long and Ger...
1912, ii. 961), which ranged from 21·5 to 27·8 mg per ..
body-weight.   It is suggested that this difference may ..
be explained by the lower muscular structure and lower ..
tone of women.   E ..

Creatine and Creatinine in Starvation. G. GRAHAM and P. POULTON (*Proc. Physiol. Soc.*, 1914, lii—liv; *J. Physiol.*, **48**, *compare* this vol., i, 228).—The results suggest that traces of creatinine only are excreted in starvation of the human subject which has lasted over three days. The excretion did not begin until forty-eight to fifty-eight hours after the last meal. Complications due to the excretion of acetoacetic acid were avoided. S. B. S.

Elimination of Phenolsulphonephthalein in Acute and Chronic Tartrate Nephritis. FRANK P. UNDERHILL and NORMAN BLATHERWICK (*J. Biol. Chem.*, 1914, **19**, 39—56).—The rate of elimination of phenolsulphonephthalein after ingestion may be greatly diminished during the acute stage of nephritis produced in rabbits by the subcutaneous injection of tartrates (A., 1912, ii, 7). In the chronic condition, the excretion of the dye is more rapid, but does not reach the rapidity associated with the normal state. When excretion by the kidney is prevented, the dye is eliminated in the fæces through the bile.

The injection of tartrates does not reduce the excretion of nitrogenous substances in the urine. Although the rate of elimination is undoubtedly diminished, the total amount of waste material excreted is unchanged. A reduced rate of elimination does not necessarily mean that the kidney is not efficient.

It has been observed in these experiments that, contrary to what is previously noted (*loc. cit.*), the glomerulus has been injured as well as the renal tubules. H. W. B.

Volatile Substances of Urine. WILLIAM M. DEHN and FRANK HARTMAN (*J. Amer. Chem. Soc.*, 1914, **36**, 2118—2136).—The characteristic odour of urine cannot be attributed to any of the single substances hitherto detected in it, and it is evident that other compounds must be present. As this subject has not been investigated systematically, the present work was undertaken.

Vapour-pressure determinations of samples of urine, from a few minutes to three weeks old, have shown that the variations of the vapour pressure with age are not large, but that in all cases the vapour pressures are lower than those of water at the same temperature.

The largest yields of volatile substances were obtained from urine by treating it with dilute sulphuric acid, leaving it for several days, and then distilling it. The distillates furnished products which were separated into four fractions, namely, acids, phenols, bases, and neutral substances. Of the acids, the principal is benzoic acid, formed by the hydrolysis of hippuric acid; the others comprise hydrogen sulphide, fatty acids up to heptoic acid, and possibly *cyclo*hexanecarboxylic acid. The phenols include *p*-cresol, and some higher compounds. The chief bases are trimethylamine and indole; traces of these occur in fresh urine and in larger quantities in fermented urine. The neutral substances contribute most largely to the characteristic odour; indications were obtained of the presence of at least four new compounds, including one (see following abstract). E. G.

Urinod, the Cause of the Characteristic Odour of ~
WILLIAM M. DEHN and FRANK A. HARTMAN (*J. Amer. Chem.*
36, 2136 – 2146. Compare preceding abstract).—The chara᥿ter᥿᥿᥿
of urine has been found to be due to the presence of
C_6H_8O, b. p. 108°/28 mm., a pale yellow oil, slightly ᥿᥿᥿
water, and possessing a very penetrating, persistent᥿ ᥿᥿᥿
odour. This substance is readily volatile with ste᥿᥿ ᥿᥿
potassium permanganate and ammoniacal silver n᥿᥿᥿᥿᥿᥿
cold, and reacts with Millon's reagent, but not with F᥿᥿᥿᥿
tion or solution of alkali picrate. The *dinitro*-deri᥿᥿᥿᥿ ᥿
78°, forms golden needles. Urinod reacts with semi᥿᥿᥿ ᥿᥿ ᥿
production of a *compound*, m. p. 254°, which crystalli᥿᥿ ᥿
hexagonal leaflets. When urinod is treated with ᥿᥿᥿᥿᥿
compounds are produced; one of these has m. p. about ᥿᥿᥿᥿
the other is not melted at 250°. The compound pro᥿᥿᥿᥿
the structure of *cyclo*hexene-4-one, $CO{<}^{CH_2 \cdot CH}_{CH_2 \cdot CH_2}$ ᥿H
quinonoid constitution $CO{<}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}{>}C$. Urinod does ᥿᥿
in the free state in urine, but exists in a conjugated form ᥿᥿
liberated by fermentation or by the action of dilute su᥿᥿᥿᥿᥿᥿
It is very toxic, and may have some connexion with urea ᥿
F᥿

The Isolation of the Substance in Butter Fat ᥿᥿
Exerts a Stimulating Influence on Growth. E. V. M᥿᥿
and MARGUERITE DAVIS (*J. Biol. Chem.*, 1914, **19**, 2᥿᥿
Compare Osborne and Mendel, A., 1913, i, 1128). The gr᥿᥿
stimulating substance present in butter-fat has been isola᥿᥿
saponifying the fat and extracting the soaps formed with ᥿᥿
ture of olive oil and ether. After removal of the ether, ᥿᥿
oil was found to have acquired growth-stimulating pr᥿᥿᥿
which were previously absent. Rats which had ceased ᥿᥿᥿
on a diet of casein, dextrin, lactose, agar-agar, and salts, ᥿᥿᥿
addition of ordinary olive oil or of cotton-seed oil, began ᥿᥿᥿
again when the above olive-oil extract of butter soaps wa᥿
to the diet.   H. W. ᥿

Pharmacological Action of Tetra-alkylammonium C᥿
pounds. I. The Action of Tetramethylammonium Chl᥿᥿
C. R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1914, **50**, 17-4᥿ ᥿
detailed account of work published previously (A., 1911, ii, ᥿᥿

Metabolism of an Isomeride of Xanthine and of ᥿᥿
Isomerides of the Methylxanthines. SAMUEL GOLDS᥿᥿
(*J. Biol. Chem.*, 1914, **19**, 83—104).—The author has studi᥿
behaviour of various purine derivatives closely related to x᥿᥿
and uric acid when injected subcutaneously into ᥿᥿
2 : 8-Dioxytetrahydropurine, an isomeride of xanthine, is exc᥿᥿
unchanged in the urine, whereas xanthine itself forms all᥿᥿
and uric acid. Uric acid, when injected subcutaneo᥿᥿
eliminated chiefly as allantoin. 2 : 8-Dioxy-6-methyl-2᥿ ᥿᥿

...thyl- and 2 : 8-dioxy-6 : 9-dimethyl-tetrahydropurines do not
...s an increase of urinary allantoin when injected subcutane-
...y into rabbits, which is in accordance with the view that
...retion is effected only with great difficulty in the body.
...ove methylated purines do not produce diuresis.

H. W. B.

Toxicity of Sodium Tartrate. WILLIAM SALANT and C. S.
...a (*Amer. J. Physiol.*, 1914, **35**. 239—264).—The toxic action
...dium tartrate has been observed in rabbits, cats, fowls, and
...n after intravenous and subcutaneous injection and adminis-
...n by the mouth. Comparatively large doses, up to 4 grams
...kilo, may be given with the food to rabbits and fowls without
...ing any toxic effect. Larger quantities cause death often
...n a few hours. Sub-acute intoxication is produced by sub-
...eous or intravenous injection of small doses, the effects being
...r to the kidney and symptoms of muscular and nervous
...bance.

...state of nutrition of the animal plays a considerable rôle
...ermining the extent of intoxication produced by a given dose
...dium tartrate. Rabbits fed on carrots are much more
...ant than those fed on oats and cabbage or on a milk diet.
...fatal dose for fasting animals may be barely toxic for those
...well fed state. Resistance seems to decrease with age.
...and *l*-Tartrates are found to be equally toxic. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

**Chemical Changes in Vegetable Organisms Undergoing
...mentation.** MARIN MOLLIARD (*Compt. rend.*, 1914, **159**,
...).—Experiments were made on the changes in the sugars and
...reous compounds in the pericarp of *Cucurbita maxima* kept
...en and in closed tubes for periods of 30, 75, and 150 days.
...th the loss of total substance and of reducing sugars soluble
...cohol was greatest in the open tubes, whilst the non-reducing
...soluble in alcohol first disappeared in the closed tube; the
...s insoluble in alcohol remained almost the same in the open
...and were only considerably reduced in quantity in the closed
...during the last period of the experiment.
...hilst the total nitrogen remained about the same, the protein
...was decreased to rather more than half in the open tube and
...than half in the closed tube. The soluble nitrogen (especi-
...ammonia) increased under both conditions, the increase
...greater in the closed tube. The amino-nitrogen remained
...ant in the open tube, and was doubled in the closed tube,
...the amide nitrogen disappeared altogether, first in the closed

N. H. J. M.

Relation of Bacterial Transformations of Soil Nitr[...]
to Nutrition of Citrous Plants. KARL P. KELLERMAN (J. [...]
Research, 1914, **2**, 101—113).—The results of pot experiment[...]
which soils from typical orange-growing areas in Californi[...]
employed showed that an excess of nitrogen as nitrates te[...]
the same symptoms of malnutrition as have been observed i[...]
areas throughout the orange belt in California. An exam[...]
of samples of soil from California showed that samples fr[...]
vicinity of deteriorating trees are richer in nitrates than t[...]
Both the poor and good soils usually contain rather [...]
amounts of insoluble nitrogen, the difference being in the rate [...]
nitrification. In pot experiments it was found that a norma[...]
of nitrification is obtained by mixing a green crop with [...]
Large amounts of mature straw are to be avoided; small [...]
of straw may, however, be applied with advantage to [...]
high in nitrates. Ground limestone, in addition, will [...] N. H. J. [...]
beneficial.

The Soluble Polysaccharides of Lower Fungi. II. My[...]
galactan, a New Polysaccharide in Aspergillus [...]
ARTHUR W. DOX and RAY E. NEIDIG (*J. Biol. Chem.*, 191[...]
235—237. Compare this vol., i, 1038).—*Mycogalactan*, C$_6$H[...]
is obtained from hot aqueous extracts of immature cultu[...]
Aspergillus niger by treatment with alcohol. The dried mat[...]
dissolves in cold water at the ordinary temperature, and [...]
the solution is immersed in a freezing mixture a transparent g[...]
is formed. It gives a faint blue colour with iodine, whi[...]
be due, however, to a trace of impurity. It has a[...] H. W. [...]
Galactose is produced by hydrolysis with dilute acid. H. W. [...]

Formation of Hexone and Purine Bases in the Autol[...]
of Glomerella. HOWARD S. REED (*J. Biol. Chem.*, 191[...]
257—262. Compare A., 1911, ii, 916).—Autolytic changes of [...]
in cultures of *Glomerella rufomaculans* result in the produc[...]
ammonia, histidine, lysine, xanthine, and hypoxanthine [...]
indication of the formation of amines could be detected [...]
dried fungous mycelium when incubated with gelatin [...] H. W. [...]
liberated lysine.

β-p-Hydroxyphenylethylamine, a Pressor Compound in [...]
American Mistletoe. ALBERT C. CRAWFORD and WALTE[...]
WATANABE (*J. Biol. Chem.*, 1914, **19**, 303—304).—The base CH[...]
previously isolated by the authors (*Jour. Amer. Med. Asso[...]
57, 865) from *Phoradendron flavescens* (mistletoe) has [...]
identified by them as β-p-hydroxyphenylethylamine. H. W. [...]

Proximate Analysis of Wheat. A. BARBIERI (*Compt.* [...]
1914, **159**, 431—434).—Twenty kilos. of wheat were washe[...]
distilled water, and the residue submitted first to maceration [...]
cold water, then extraction with warm water (50—60°), and [...]
with boiling water. The residue from this treatment was se[...]

of the portion passing through was treated with absolute alcohol, finely granular, homogeneous, white flour (M) being obtained filtration. The portion remaining on the sieve was similarly ated with alcohol, filtered, and the filtrate kept. The aqueous tracts obtained with boiling and warm water were separately concentrated on a water-bath, and then alcohol was added, the precipitates, a and β, being filtered off. These two filtrates were and with those from M, and from the residue on the sieve, the which was distilled off, and the aqueous residue (C) shaken with chloroform. The filtrates from the first two treatments with water are also shaken with chloroform after concentration. The three separate chloroform extracts so obtained were mixed, and on distilling off the chloroform, the residue, after treatment first with ether and then with alcohol, yielded from the second solvent grams of a yellow colouring matter, which was probably a physiological transformation product of chlorophyll. It did not give either the biuret reaction or the reaction for acraldehyde, was soluble in water, but soluble in benzene, carbon disulphide, or in petroleum. The aqueous layer from C was treated with acid until a slight precipitate appeared, and then dialysed, and in the dialysed liquid monopotassium phosphate and potassium phosphate were obtained, but no monocalcium phosphate.

The flour M, together with the precipitates a and β, on extraction with ether, gave an oil, of which the major portion was insoluble in acetone, and contained no phosphorus, sulphur, or nitrogen, and the smaller, soluble portion, 8 grams, contained 1 gram of phosphorus, thus proving the non-existence of lecithins in the wheat. By incinerating the flour M, and also the residue on the sieve, they were found to contain, respectively, 0·30 and 0·62% of insoluble salts, consisting chiefly of calcium sulphate and tricalcium phosphate, but no carbonates.   W. G.

The Organic Phosphoric Acid Compound of Wheat Bran. R. J. ANDERSON (*J. Biol. Chem.*, 1914, **18**, 425—440. Compare A, 1912, ii, 1205).—The author shows that the organic phosphoric acid compounds obtained from wheat bran by the usual methods are contaminated with oxalates and inorganic phosphates. Purer preparations have now been obtained by precipitation from very dilute hydrochloric acid with alcohol. Several amorphous barium salts have been prepared; also an amorphous silver salt, which darkens very rapidly, and finally turns quite black. These compounds are quite different from the corresponding phytates. Evidence is adduced to show that wheat bran contains several organic phosphoric acids differing so slightly from one another that their separation is very difficult.   H. W. B.

The Organic Phosphoric Acid Compound of Wheat Bran. II. Inositol Monophosphate, a New Organic Phosphoric acid Occurring in Wheat Bran. R. J. ANDERSON (*J. Biol. Chem.*, 1914, **18**, 441—446. Compare preceding abstract).—Inositol monophosphate is prepared from the hydrochloric acid extract of

wheat bran by treatment with barium hydroxide, filtering the precipitate, and, after removing excess of barium, concentrating in a vacuum and precipitating with alcohol. The substance is purified by means of its insoluble lead salt. After recrystallisation from water, with the addition of alcohol, it was obtained in colourless, star-shaped aggregates of plates or prisms.

Inositol monophosphate, $C_6H_6(OH)_5 \cdot O \cdot PO(OH)_2$, when heated rapidly in a capillary tube, softens at 200°, and decomposes at 201—202°. When slowly heated, it softens at 188°, and melts at 190—191° (decomp.). It is optically inactive. It is very soluble in water, giving an acid solution, but is insoluble in alcohol and the usual organic solvents. In the cold, no precipitate is produced with copper acetate, but on warming the solution, a bluish-white precipitate separates, which again dissolves completely on cooling. After hydrolysis with sulphuric acid or ammonia in a sealed tube, inositol and phosphoric acid were isolated and identified.

H. W. B.

Is Silica an Indispensable Constituent of Plant Food? MARSHALL LUNDIE (*S. African J. Sci.*, 9, No. 10; *Chem. News*, 1914, 110, 200—202).—Water culture experiments with wheat supplied with the usual nutrients, but without silica. The dry leaves and stems contained, respectively, 1·212 and 0·347 % silica.

Reference is made to a previous experiment, by Hahn, in which wheat grown under similar conditions was attacked by rust, the plant being overrun with the fungus in two days.

It is suggested that whilst silica is not an essential plant food for cereals, it may be of use in enabling the plants to resist attacks of fungoid growth. If this is correct, cereals grown on basalt and basalt soils should suffer less from fungoid attacks than those grown on granite soils, climatic and weather conditions being the same (compare Hall and Morison, *Proc. Roy. Soc.*, 1906, B, 7, 455).

N. H. J. M

[Influence of Zinc, Copper, Manganese and Cerium on the Growth of Wheat.] J. A. VOELCKER (*J. Roy. Agric. Soc.*, 1913, 74, 411—427. Compare A., 1913, i, 1430).—Experiments with wheat grown in pots containing 40 lbs. of soil. Zinc was applied at the rate of 0·01, 0·02, and 0·03% in the form of phosphate, nitrate, and carbonate; copper (0·0025, 0·005, 0·025, 0·05, and 0·1%) as sulphate and carbonate; manganese as phosphate and carbonate, and cerium as oxide and sulphate (0·1, 0·025, and 0·005%).

As regards zinc, it was found that the larger amounts of nitrate retarded germination, whilst the other salts were almost without effect on germination and in the earlier stages of growth. Later in June, a toxic effect was shown in the case of the larger amounts of carbonate and phosphate, and especially with nitrate, which caused the tops of the ears to be practically "blind." The final results showed a reduction in the yield of grain, except with 0·01

as nitrate, and, coincidently, a more or less considerable of straw (except with the largest amount of nitrate); with of zinc as nitrate the yield of straw was nearly doubled, the lowest gain, with 0·03% as carbonate, was 29%. Zinc phate and carbonate increased the root development, which very stunted when nitrate was employed.

The conclusions drawn from the copper experiments are that dilation occurs when the application is between 0·01 and 0·02%; larger amounts are toxic, and that smaller amounts are without effect. The greatest gain (straw 79 and grain 62%) was used with 0·02% of copper as carbonate. With the beneficial curts of copper, especially with the sulphate, the roots were extensive and fibrous as compared with untreated plants.

The results obtained with manganese and cerium were negative, indications of stimulation or of toxicity being obtained.

N. H. J. M.

Occurrence of Hydrogen Cyanide in Millet and Guinea Corn. R. FURLONG (*Analyst*, 1914, 39, 430—432).—See this vol., ii, 821.

Occurrence of Methyl Alcohol in Maize Silage. E. B. HART A. R. LAMB (*J. Amer. Chem. Soc.*, 1914, 36, 2114—2118).— Hart Willaman (A., 1912, ii, 1205) have found that maize silage gains a small amount (about 0·05%) of methyl alcohol, whereas x and Neidig (A., 1913, i, 236) have stated that this alcohol is absent.

Several samples of maize silage have now been examined, and all cases the presence of methyl alcohol was detected. As a number of different tests were employed for identifying the methyl alcohol, the possibility is precluded of the reactions being due to some other substance.

E. G.

Lucerne. V. Enzymes Present in Lucerne. C. A. JACOBSON August HOLMES (*J. Amer. Chem. Soc.*, 1914, 36, 2170—2182).— an earlier paper (A., 1913, i, 151) an account was given of the enzymes present in the seeds of lucerne (*Medicago sativa*). A tentative study has now been made of the enzymes in (*a*) the dried stems and leaves, (*b*) the fresh stems and leaves, and (*c*) the roots. The following enzymes have been detected. In (*a*), raisin and pectinase in large quantities, invertase and protease (peptolytic), and small quantities of amylase and peroxydase. (*b*), emulsin and pectinase in large quantities, coagulase, peroxydase, and protease (peptolytic), and small quantities of amylase, and invertase. In (*c*), peroxydase in large amount, coagulase, invertase and pectinase, and small quantities amylase and emulsin.

E. G.

Experiments with Tomatoes. J. A. VOELCKER (*J. Roy. Agric. Soc. Eng.*, 1913, 74, 419—422).—Pot experiments with tomatoes in artificial soil consisting of rotted turf, sand, and limestone, both in its natural state and after being heated in a moist con

dition at 80—100°. To some pots lithium phosphate (L. ...)
and 0·005%) was added, whilst others received magnesia ... ...
amounts that the total magnesia in the soil was raised ... ...
to 0·792, 1·188 and 1·584 respectively. The highest amount ...
magnesia was practically equal to the lime present in the ...

The effect of heating alone was to raise the yield of ... ...
Addition of 0·002 and 0·005% of lithium to the unheated ...
reduced the yields to 29 and 37% respectively of the amount ...
obtained in soil alone. In the heated soils with lithium the ...
were 71 and 14%. So that the toxic effect of the smaller amount ...
of lithium was much reduced by heating the soil, whilst with ...
larger amount the toxic action was more marked in the heated ...

As regards magnesia, the normal soil containing 1·188 ... ...
an increase of 13% over the unmanured soil, whilst in those con-
taining 0·792 and 1·584% the yields were respectively reduced ...
89 and 12%. In the heated soils containing 0·792% of magnesia ...
the yield was 31% over that of the unheated soil without added ...
magnesia; with 1·584% of magnesia in the heated soil the yield ...
was only 22%. Magnesium carbonate gave similar results to the ...
oxide.

As compared with wheat, tomatoes are more affected by lithium
and magnesium.   N. H. J. M.

**Comparative Efficiency for Milk Production of the Nitro-
gen of Lucerne Hay and the Maize Grain. Effect of Diuresis
on Milk Secretion.** E. B. HART and G. C. HUMPHREY with
J. J. WILLAMAN and A. R. LAMB (*J. Biol. Chem.*, 1914, 19, 237—265.
Compare A., 1913, i, 151).—Further experiments on heifers show
that the nitrogen of lucerne hay is as effective as that of the maize
kernel for the formation of the milk proteins.

Lucerne hay has specific diuretic properties. The increased
renal activity observed when it is employed as a constituent of the
food is associated with a corresponding diminution in the flow of
milk. The diuretic stimulus causes in some cases a shrinkage of
volume of 2·5—2·75 kilos. of milk in a flow of 11·5 kilos. day. It
has not been ascertained whether salts or specific substances of
organic nature in the hay are responsible for the diuretic action.
                                                    H. W. B.

Flavour of Roquefort Cheese. JAMES N. CURRIE (*J. Agric.
Research*, 1914, 2, 1—14).—During the ripening of Roquefort cheese a
considerable amount of the fat is hydrolysed, the chief factor in
the hydrolysis being a water-soluble lipase produced by *Peni-
cillium roqueforti*. The result is an accumulation of the acids of
milk fat, both free and combined.

The peppery flavour of the cheese is due to hexoic, octoic, and
decoic acids, and their readily hydrolysable salts.
                                                    N. H. J. M.

Humic Acids. BR. TACKE, A. DENSCH, and TH. ARND (*Landw.
Jahrb.*, 1914, 45, 195—265).—A reply to Gully (*Mitt. k. bayr. Moor-
kulturanst*, No. 5), in which the behaviour of peat towards titration

......ate, sodium acetate and other salts, calcium oxalate, ...ium and ferric chlorides, and colloidal ferric hydroxide, the ......ation by water of absorbed bases from *Sphagnum* and peat, ... electric conductivity, the iodine reaction, the inversion of ...... by peat, and the liberation of hydrogen in presence of iron ...... peat, are discussed. The results are opposed to the view that ...... are due to colloid adsorption, and not to the presence of ......

N. H. J. M.

Selective Adsorption (by Soils). E. G. PARKER (*J. Ind. Eng.* ...... 1914, **6**, 831—835).—Soils have not only the power of ad-...... dissolved salts from solution, but also of adsorbing one ...... at a greater rate than the other; the nature of the surface ...... the constituents of a soil is such that the cation is adsorbed at ...... much greater rate than the anion. The presence of bases ...... magnesium, etc.) in solution, after contact of certain ...... solutions with a soil, is not due to direct chemical reaction ...... the salt with the silicates of the soil, but to a secondary reaction ...... the free acid, resulting from the selective adsorption of the ...... with the mineral constituents of the soil. Generally, the ...... the soil particles, the greater the selective adsorption of ...... cation. The adsorption of the cation increases with the con-...... of the solution up to a certain point, and then remains ...... constant. At very low concentrations the adsorption ...... the cation is complete. The presence of other substances may ...... may not affect selective adsorption by a soil.   W. P. S.

Occurrence of Aldehydes in Garden and Field Soils. ...... SCHREINER and J. J. SKINNER (*J. Franklin Inst*, 1914, **178**, ... 343).—Experiments in which a large number of soils were ...... with 3% sodium hydroxide, and the extracts, after being ...... with acid to remove the humic acids, examined for alde-...... Physiological tests were made with the aldehydes by means ...... wheat seedlings, and when possible qualitative tests with ferric ...... and magenta reagent were made. The soils included ...... garden and greenhouse soils which had failed to grow ...... crops, and sixty field soils.

Of the unproductive garden soils, five contained aldehydes; out ...... unproductive field soils, nine contained aldehydes; and ...... of the same number of productive soils, three contained ...... hydes.

Aldehydes were found in neutral, acid, and alkaline soils, mostly ...... soils. No relation seems to exist between the crop being ...... or the type or texture of the soil and the presence of alde-...... The presence of aldehyde is not confined to any locality, ... found as far apart as New York and Mississippi.

The effect of the extracted aldehyde material on the growth of ...... varied from slightly, to very, harmful. Of the extracts in ...... aldehydes were not found, nineteen were without effect, ... were injurious, and fourteen beneficial or slightly so.

N. H. J. M.

Action of Manganese in Soil. J. J. SKINNER and I. SULLIVAN (*U.S. Dept. Agric.*, *Bull.* No. 42, 1914).—The results of experiments in which wheat was grown in an unproductive loam, both without and with addition of manganese (as sulphate, nitrate, carbonate, and dioxide), showed a good effect when the salt was applied in amounts from 5 to 50 per million. On a productive loam, manganese salts were of no effect.

In further experiments on the action of manganese on the growth of wheat in aqueous extracts of soils, and the oxidising power of the plants, it was again found that there was increased growth and oxidation in unproductive soils; in productive soils there was increased oxidation, whilst the growth was decreased.

Finally, a field experiment is described in which wheat, maize, cowpeas, and potatoes were manured with manganese sulphate (56 kilos. per hectare). It was found that manganese sulphate decreased both the crop and the oxidising power of the soil, which was an acid one.

The conclusion is drawn that the beneficial action of manganese may be due to increased oxidation, resulting in the destruction of injurious products in the soil, whilst the injurious action in case of good soils may be due to excessive oxidation.

Acid soils, which are unfavourable to oxidation and nitrification, do not seem to be benefited by manganese.   N. H. J. C.

Sulphur as a Fertiliser. J. A. VOELCKER (*J. Roy. Agric. Engl.*, 1913, **74**, 419).—Applications of flowers of sulphur at the rate of 3·36, 6·72, and 13·44 kilos. per hectare, were made on mustard, rape, and clover grown in pots. The sulphur was mixed with the last portion of the soil used to fill the pots.
                                                      N. H. J. C.

Influence of Sulphur on Soil Acidity. H. CLAY LINT (*J. Ind. Eng. Chem.*, 1914, **6**, 747—748).—In order to ascertain the rate of oxidation of sulphur in soils, 100-gram portions of soil were treated with 33 mg. of sulphur (equivalent to 1000 lb. of sulphur per foot), and the moisture content was adjusted at 20%. The acidity of the soils increased gradually, as shown by the Jones acetate method, up to the eighth week, when all the sulphur was oxidised. Sulphur is oxidised more rapidly in heavy clay soils than in sandy loam soils (compare A., 1913, i, 811).
                                                      W. P.

General and Physical Chemistry.

...rum of the Oscillatory Discharge in Various Gases.
BRUNETTI (*Nuovo Cim.*, 1914, [vi], **7**, i. 390—410).—The
... has investigated the spectra of the oscillatory discharge
... between magnesium electrodes in hydrogen, oxygen,
...en, and carbon dioxide. The first part of the discharge
... lines of the gas and of the metal of high and low excitation;
... second part, the metallic lines of low excitation remain, and
... accompanied by the bands of the gas and of the compounds
... latter with the metal. The bands start from the positive
... and cease at a distance from the negative one, whilst the
... traverse the whole space between the electrodes, and the
... lines are not found in the regions bordering on the elec
... The first phase of the oscillatory discharge presents,
... those complex phenomena known as a spark; it opens the
... ionising the gas, carries with it occasional particles of the
... and heats the electrodes to redness, being then replaced by
... second phase of the discharge, namely, the arc. In the latter
... a localisation of the seat of emission of the various series
... the principal series originating in a stratum surrounding
... series emitted by the central regions. The heating
... electrodes during this second part of the discharge depends
... thermal conductivity of the surrounding medium; in
...gen, the heating does not last so long as in nitrogen, oxygen,
... dioxide, whilst the discharge is extinguished sooner. The
... change in potential at the electrodes falls off in the adjacent
... for equal magnitudes of the auto induction, the difference
...ntial at the electrode is greater in oxygen than in nitrogen,
... least in hydrogen. The luminous emission is subjected to
... of the gas in which the discharge takes place, since the
... to some extent both the distribution of the electric
... interposed between the electrodes and the temperature of the
... ...

T. H. P.

...rk Spectrum of Nickel under Moderate Pressures.
...BUHAN (*Phil. Trans.*, 1914, [*A*], **214**, 359—371).—The influence
...sure on the spark spectrum of nickel has been examined
...sures up to eleven atmospheres. One of the most striking
... of the increase of pressure is the change in the character
... ...nes, which, according to the differences in behaviour, may
...ided into five groups. These groups contain, respectively,
... which show symmetrical reversion; (2) lines which reverse
...etrically; (3) lines which remain bright and sharp;
... which remain bright, but are symmetrically broadened;
...es which are unsymmetrically broadened towards the red.
...neral effect of an increase of pressure on the relative intensi-

ties of the lines is similar to that produced by the ....
self-induction in a spark circuit.

All nickel lines are displaced towards the red, the ....
being the same for lines of the first and second groups ....
shifts are larger for unreversed lines, and are greater ....
which broaden unsymmetrically towards the red.

The observations point to the existence of two ....
λ 3514·14 and λ 3608·98, the wave-lengths of which are ....
identical with those of nickel arc lines.   H. M.

The Infra-Red Absorption Bands of Hæmoglob:.
HARTRIDGE and A. V. HILL (*Proc. physiol. Soc.*, 1914, ...
Physiol., **48**).— The absorption spectrum of reduced oxy ...
hæmoglobin was measured by means of a very ....
photometer. It was found that the absorption by ....
greatest, by oxyhæmoglobin less, and by the car.....
still. The differences are sufficiently great for it to ....
employ the method for determining the amount ....
pounds present in a given solution.   S. I

Simple and Complex Rotatory Dispersion   T. M.
LOWRY and T. W. DICKSON (*Trans. Faraday Soc.*, 1914, **10**. ..
Compare P., 1913, **29**, 185). All cases of rotary ..
may be represented by Drude's formula. Simple ....
persion may be expressed by the equation a ....
complex rotatory dispersion requires two or more ....
which may be negative. Anomalous dispersion is ....
many instances to dynamic isomerism.   C. B

An Enclosed Cadmium Arc for Use with the Polar:.
T. MARTIN LOWRY and H. H. ABRAM (*Trans. Faraday Soc.*
10, 103—106).— For substances with simple rotatory disper-..
preceding abstract), measurements with light of two ...
such as the green and violet mercury lines, are suff....
mine the form of the dispersion curve. For more ....
cadmium arc may be used. The arc passes between ....
electrodes of solid cadmium in a vessel exhausted by ....
Gaede pump. When the vacuum is good, the arc will ....
start itself, but usually the passage of a spark from ....
is necessary There is a silica bridge between the ....
the tube has two quartz windows.

a- and β-Methylglucoside show simple rotatory disper-
ratios for the violet and green mercury lines being the ....
the green and red cadmium lines.   C. B

The Constitution of Liquid Mixtures and Their Rota
Power.   A. COTTON (*Trans. Faraday Soc.*, 1914, **10**, ...
The determination of the optical rotatory power and of the
netic birefraction of the same mixture of liquids is pro....
means of determining whether complexes are present.   C. B

Rotatory Power of Mixed Crystals, NaClO₃-AgClO₃. P. PRITCHA (*Atti R. Accad. Sci. Torino*. 1914, **49**, 1127—1134. Compare Retgers, A., 1890, 1208; Foote, A., 1902, ii. 453).—The rotation of mixed crystals of sodium and silver chlorates varies for among crystals from one and the same crystallisation, and from sector to sector of an individual crystal. The crystals show various optical anomalies, the double refraction of two increasing with the content of silver chlorate. The specific gravities have been measured, and are found to be in accord with Retger's additive law. Monometric silver chlorate has an approximately constant specific gravity of about 4·20 in mixed crystals of all compositions, and its specific rotation is 12·65°, i.e. about four times that of sodium chlorate.   T. H. P.

Optical Activity of Chemical Compounds without Carbon. A. WERNER (*Compt. rend.*, 1914, **159**, 426—429).—The author has prepared an optically active compound containing no carbon but similar in composition to the cobalt triethylenediamine (Co en₃)X₃, en representing NH₂·CH₂·CH₂·NH₂. In place of one molecule of ethylenediamine there is in the new compounds the molecular complex [(OH)₂Co(NH₃)₄]X, their asymmetric constitution being represented by

en   en

en   en
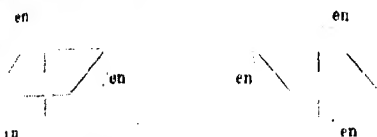
salts prepared were the *bromides*, having the composition [(H₄Co(NH₃)₄)₃)Br₆,2H₂O, the active forms being prepared by crystallisation from their π-bromocamphorsulphonates with sodium bromide. The active *d*-salt prepared in this way crystallises in greyish-brown plates and is very soluble. It has [α]₅₀ varying from 4000° to 4500°, its rotatory power diminishing rapidly in aqueous solution, the salt becoming inactive after two hours.
W. G.

Existence of Racemic Tartaric Acid in Solution. T. M. LOWRY (*Trans. Faraday Soc.*, 1914, **10**, 80—83. Compare A., ii. 747).—When *d*- and *l*-tartaric acids are mixed in unequal proportions in solution, the measured rotatory dispersions are those that would be expected if the two acids remained uncombined. Mixtures of *d*-tartaric acid and racemic acid also behave in solution as if the latter compound were dissociated into its components.
C. H. D.

Rotatory Power of Tartaric Acid. G. BRUHAT (*Trans. Faraday Soc.*, 1914, **10**, 84—90).—The rotatory power of fused and supercooled tartaric acid has been observed at temperatures from 180° downwards, and for light of different wave-lengths. The dispersion is normal at 180°, but becomes anomalous below 100°.

54   2

The dispersion curves are plotted together with those determined by Arndtsen (*Ann. Chim. Phys.*, 1858, [iii], **54**, 403 for the solutions of various concentrations, and exhibit a similarity. The only hypothesis which will account for the phenomena is that of the presence of two compounds of opposite rotatory power, in proportions varying with the temperature and concentration, in both the solutions and the undercooled melt of these compounds being ordinary tartaric acid, the other being be a complex aggregate.

Cryoscopic determinations in water by acetic acid show that quantity of the polymeride cannot much exceed 2 per cent, and have a rotatory power of from −80° to −200°. This is comparable with the rotatory power of solid rubidium tartrate.

                          C. H.

Discovery of the Sensitiveness of Silver Salts to Light.

Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1914, **49**, 1043). The author regards Homberg's observation in 1694 (compare this vol., ii, 234) as of little importance, since it refers to nitrate in contact with organic matter, which accelerates the composition of the silver salt, and since also it was known earlier, before the time of Boyle (1663), that silver salts in the light or in the air. Of far greater importance development of photography were the investigations of (1727), and particularly those of Beccari (1757) and Scheele The invention of the dark chamber is due to G. B. Porta 1540—1615).

                          T. H.

Radium Constants on the International Standard.

Ernest Rutherford (*Phil. Mag.*, 1914, [vi], **28**, 320). A recalculation of the radioactive magnitudes in the "Radioactive Substances and their Radiations" is given on the basis of the International Standard. The equilibrium of radium to uranium is now $3 \cdot 23 \times 10^{-7}$, the yearly production of helium per gram of radium, calculated 163, found 164 ; the total observed heating effect per gram of radium in equilibrium with its first four products is 134·7 calories per hour, made up of radium, 25·1; emanation, 28·6; radium-A, 30·5; *B* and *C*; the equilibrium volume of emanation per gram of radium calculated, 0·62, found 0·63 cu. mm.; number of α-particles expelled per second per gram of radium, itself, $3 \cdot 57 \times 10^{10}$, in equilibrium with first four products, $14 \cdot 3 \times 10^{10}$; the total positive charge, the latter case, 33·2 *E.S.U.*, or $1 \cdot 11 \times 10^{-3}$ *E.M.U.*; the negative charge carried by the β-particles of radium *B* and *C* 18·3 *E.S.U.*; the total saturation current due to α-rays from of emanation, itself, $2 \cdot 89 \times 10^{6}$ *E.S.U.*, and with its products $9 \cdot 94 \times 10^{6}$.

With regard to the heating effect of the emanation calculated from the kinetic energy of the α-particles expelled is 7% lower than the observed, the following explanation suggested. The energy of the electronic distribution of an atom

expected to increase with increase of the nuclear charge, or the mass of the α-particle may be expected to be accompanied by increase of the energy of the electronic distribution, and the expulsion of the β-particle by the opposite effect. The relative heat effect of radium-B and -C, as compared with that of the radium and radium-A, is less than the calculated, in agreement with this view, since β-rays as well as α-rays result in the change radium-B and -C. It is calculated that of the total heat effect of the α-ray changes, some 90% is due to the kinetic energy of the α-particle expelled and 10% to loss of internal atomic energy in manner indicated.

From the value for $nE = 1·11 \times 10^{-9}$ E.M.U., where n is the number of α-particles per gram per sec. of radium itself, and E is the charge each particle carries, the half-period of radium on the International Standard is 1690 years. The experimental determinations give 2000 years (Boltwood), 1800 years (Keetman), 1730 (Stefan Meyer).

F. S.

Mass and Velocities of α-Particles from Radioactive Substances. Sir E. RUTHERFORD and H. ROBINSON (*Phil. Mag.*, vi, **28.** 552—572).—From the mean of recent determinations of atomic weight of helium, 3·998, and the value of e/m for the hydrogen atom, 9570, the value of e/m for the α-particle, or helium carrying two positive charges, should be 4826, whereas the best experimental value is 5070. To test as thoroughly as possible whether the value of e/m for a high-speed positive particle equals the value from electrochemical data, experiments have been made, to an accuracy of 1%, on the value of e/m of the α-particle by measuring the deflexions of a narrow pencil of α-rays as given by the photographic method, in very carefully determined electromagnetic and electrostatic fields. The final results for the value of e/m of the α-particles of radium emanation, radium-A and radium-C, lay between 4813 and 4826, the mean value being which agrees with the calculated result within the limits of

The initial value of the velocity of the α-particles of radium-C is $1·922 \times 10^9$ cm. per second, about 7% lower than the usually accepted value. On the new data, the development of heat calculated from the kinetic energy of the α-particles for radium and its products is 7% less than the observed, and part of that effect is probably due to other sources (see preceding

special search was made for atoms differing from the α-particle in mass or charge, and the conclusion is drawn that if any exist their number is certainly less than 1 in 10,000 of the number of α-particles.

F. S.

Connexion between the β- and γ-Ray Spectra. Sir ERNEST RUTHERFORD (*Phil. Mag.*, 1914, [vi], **28**, 305–319).—Previous investigations on the β- and γ-rays are discussed from the point of the general problem of radiation, and tentative conclusions. The results of Chadwick (this vol., ii, 408) show that even

the intense lines in the magnetic spectrum of radium B are a small fraction only of the total β-rays emitted. From it seems that β-ray magnetic spectra are probably continuous a superimposed line spectrum. The continuous spectrum ascribed to the escaping β-particle suffering in its egress the nucleus of the atom several collisions of the ordinary with the electrons in the outer electronic distribution of the atom In addition, it is supposed that certain well-defined regions part of the atom are set into definite vibration, whence "characteristic" γ-radiations of the atom arise and one or groups of β-rays of definite speed are expelled, which give the spectrum observed. The conclusion that characteristic γ-rays a line spectrum of β-rays must accompany one another out by the evidence. Radium-E, which gives only a continuous β-ray spectrum, gives little or no γ-radiation.

To explain their absence in such particular cases, the conclusion is drawn that the direction of expulsion of the β-particle from nucleus with regard to the structure of the atom must and be the same for all the atoms. Thus if this direction lie through one of the vibrating regions of the atom before lated, neither γ-radiation nor "line" β-radiation is emitted same explanation covers the remarkable anomalies exhibited the types and relative intensities of γ-rays emitted by the radio-elements. In the bombardment of atoms by cathode ray sufficient speed, however, the rays enter the atoms in all directions and all types of characteristic X-rays have a chance excited.

Accepting Planck's relation between the frequency and of radiation and his values for the numerical constant and electronic charge, the experimental evidence is reviewed from point of view differing from that before propounded. The effect of the ejection of the β-particle from the nucleus excitation of γ-rays at one vibrating region of frequency the energy of these γ-rays suffers partial or complete into energy of "line" β-radiation in the same region or vibrating region of frequency v_2. The energy of the β particle these cases will be either phv_1 or $phv_1 - qhv_2$, where p and q integers and h is Planck's constant. On comparing the energy the lines in the β-ray spectrum of radium-B and C with the frequency of the γ-rays, numerous close agreements are found which can hardly be accidental. Thus the unit of energy $0.4284 \times 10^{13}e$, which enters as an integral multiple in the Nos. 1 to 29 (A., 1913, ii, 899) of the β-ray spectrum of radium is, within the experimental error, one-third of 1.25×10^{13} energy of one of the strong lines of the γ-ray spectrum of radium reflected from rock-salt at an angle of $1°0'$, as deduced by Planck's relation. Of twelve strong lines of the β-ray spectrum, the energy of six are multiples of $1.285 \times 10^{13}e$, and thirteen (including of the first six) are multiples of another unit, 0.74×10^{13}, corresponds with the line reflected by rock-salt at $1°46'$ γ-ray spectrum of radium-B and C, and is believed to be

one component belonging to each radio-element. The two lines not so included in the β-ray spectrum correspond with and ten times a third unit, 1.75×10^{18}, which again corresponds with the γ-ray line of shortest wave-length yet observed, that reflected from rock-salt at an angle of 0·43'.

With regard to the β-ray spectrum of radium B, the evidence similar, but less conclusive, on account of the large number of the γ-ray spectrum. Two of the strong lines are expressed as multiples of 0.870×10^{15}, to be expected of the γ ray reflected at 1·24'. But the γ-ray lines reflected at 10° and do not appear to be responsible for any of the β-rays.

Many some as yet untested deductions on the relation between spectra of β-rays excited by characteristic X rays and the length of the latter are drawn.   F. S.

Number of Ions Produced by the β- and γ Radiations of Radium H. G. J. MOSELEY and H. ROBINSON (*Phil. Mag.*, 1914, **28**, 327–337).—The total number, N, of pairs of ions produced per sec. by the γ-rays of radium B and C in equilibrium with gm. of radium is determined to be 1.22×10^{15}, whereas the α rays alone produce 8.46×10^{15}. The ratio between these quantities is 6·94·1, whereas the heating effects observed are 6·4 and cal. per hour. In the following table the values of N, the heating effect, and the average energy emitted, per atom, are given for the β and γ rays of radium-B and C:

	$N/10^{15}$	Heating effect (cal. per hour)	Average energy per atom ($\times 10^{-6}$ erg.)
β rays of radium-B	0·325	1·71	0·55
γ rays of radium-C	0·64	3·35	1·09
β rays of radium-B	0·084	0·44	0·14
γ rays of radium-C	1·134	5·96	1·94
β and γ rays of radium-B	0·41	2·15	0·70
β and γ rays of radium-C	1·774	9·3	3·02

In Rutherford's original theory, the figures in the last two lines of the last column should be the energy of the β-particle which has got without exciting γ radiation. In the case of radium C, some few β particles with energy as high as 3.9×10^{-6} erg. were observed. In the case of radium-B the fastest β-ray gives the energy 0.6×10^{-6} erg.   F. S.

Secondary γ-Radiation D. C. H. FLORANCE (*Phil. Mag.*, 1914, **28**, 363–367. Compare this vol., ii, 160). Using equal masses and area of thin radiators, carbon, aluminium, copper, zinc, tin, and the amount of γ-radiation scattered by the radiator is the same after it has passed through 0·084 cm. of lead. After passing through 0·202 cm. of aluminium the lead radiator produced more scattered radiation than the others. This extra radiation from lead is probably a characteristic radiation. The scattering seems to be simply proportional to the number of electrons in the atom or to the weight of the atom, an electron in a light

aluminium atom scattering to the same extent as one ⟨?⟩
atom of lead. The loss of energy by the γ-ray to the ⟨?⟩
increases with the angle of scattering, and the penetrat⟨?⟩
of the scattered radiation depends essentially on the ⟨?⟩
scattering and not on the material of the radiator.

F.

The Distribution of Energy in the Different Types of
Rays Emitted from Certain Radioactive Substances. ⟨?⟩
JADWIGA SZMIDT (*Phil. Mag.*, 1914, [vi], **28**, 527—5⟨?⟩
determination of the total number of ions each typ⟨?⟩ ⟨?⟩
duces in air or other gases gives the ratio of the ener⟨?⟩
different types if it is assumed that the same propor⟨?⟩
energy of different rays is spent in ionisation and that th⟨?⟩
required to produce an ion is the same for γ-rays of dif⟨?⟩
penetrating power. To test the second point, the total ⟨?⟩
in various gases by γ-rays of different hardness was deter⟨?⟩
For the soft γ rays of radium-*D* the ionisation produced ⟨?⟩
dioxide, carbon dioxide, and air is proportional to the ab⟨?⟩
in these gases, but in the case of hydrogen sulphide greater ⟨?⟩
tion is produced, as is the case also with *X*-rays. In the case
the hard γ rays from radium-*B* and radium-*C*, the ionisa⟨?⟩
proportional to the absorption.

Of the total γ-ray energy of radium-*D*, the hard γ rays ⟨?⟩
between 17 and 35%. In the γ-rays of radium-*B* and *C* the
energies of the soft rays of radium-*B*, the hard rays of radium
and the rays of radium-*C* are estimated as in the ratio
1 : 45 : 639.

F.

Ordinals or Atomic Numbers? A. VAN DEN BROEK (*Phil. M⟨?⟩*,
1914, [vi], **28**, 630—632).—The author criticises Rydberg's sugg⟨?⟩
tion (this vol., ii, 599) that the frequencies of the *X*-rays
are related to the "ordinals" which are two units higher than the
atomic numbers. The hypothesis that the frequencies are rela⟨?⟩
to the atomic numbers affords a more satisfactory account of the
experimental results, and also affords a basis for the explanation
of observations on the scattering of α-particles and of Rutherford's
H. M. D.

The Absorption Coefficients of *X*-Rays. W. H. BRAGG and
S. E. PEIRCE (*Phil. Mag.*, 1914, [vi]. **28**, 626—630.—The
method of determining the wave-lengths of *X*-rays by reflection
from crystal surfaces has made it possible to determine the relation
between wave-length and absorption coefficient. The waves
examined are those emitted by anti-cathodes of silver, palladium,
and rhodium, each of which yields a spectrum consisting mainly
of two well-defined intense lines. Each wave-length was isolated
by reflection from a rock-salt crystal, and its absorption coefficient
in various metals determined. Barkla's rule that the ratio of
absorption coefficients is independent of the wave-length of the
rays is confirmed over a wide range.

Tho results suggest that the absorption coefficient of any ⟨?⟩

...ce of atomic number N is equal to CN^4, where C has constant ...over prescribed ranges.   The constant changes its value ...ely in passing through the wave-lengths of the Rh–Pd–Ag ...p examined.   According to Darwin, the absorption coefficient ...as the 5, 2 power of the wave-length of the rays absorbed, ...this, combined with the preceding, gives the very general rule ...the atomic absorption coefficient, defined as the proportion of ...energy of the X-ray pencil which is absorbed on crossing a ...re on which lies one atom to every square centimetre, is ...', where λ is wave-length of the X-ray, C is equal to ... C for all values of N between 13 (Al) and 46 (Pd), and to ... C for all greater values.   F. S.

Effect of X-Rays on the Action of Certain Enzymes.   A. ...ans (*Amer. J. Physiol.*, 1914, **35**, 224—238).—The author ...des experiments which indicate that a short exposure of ...st, diastase, and other enzymes to X-rays increases the activity, ...f the exposure be prolonged for more than five minutes the ...e w to diminish the activity of the enzyme.   Between these ...extremes there lies a point at which the radiation is ineffective. ...accelerating and the inhibiting effects are slight, but seem to ...finite.   H. W. B.

Experiments on the Active Deposit of Radium.   E. M. ...well (*Phil. Mag.*, 1914, [vi], **28**, 417 ; *Amer. J. Sci.*, 1914, [iv], ... 83 304.   Compare A., 1913, ii, 905).   In a series of experi- ...on the distribution of the active deposit from radium emana- ...n ethyl ether, it was found that neither a positive nor negative ...ntial exerts any appreciable effect, the proportion reaching the ...ga electrode of a cylindrical vessel being 10%.   Hence the ...les of active deposit at the end of their recoil paths in ether ...charged, the amount reaching the electrodes arriving there ...fusion.

When the emanation in relatively large quantity is mixed with ...the active deposit particles in the gas form large aggregates ...h acquire positive and negative charges from the ions present ...he gas.   The formation of these aggregates appears to cease ...rly when the concentration of the emanation and the degree ...sation it produces sink below a certain value.   Under these ...ditions, the particles in the gas are practically all neutral, and ...h the electrodes through simple diffusion, the diffusion coeffi- ...t in dry air at atmospheric pressure and about 20° being ...ximately 0·045 cm.² sec.⁻¹.   F. S.

The Distribution of the Active Deposit of Radium in ...ctric Fields.   H. P. WALMSLEY (*Phil. Mag.*, 1914, [vi], **28**, ...—351.   Compare A., 1913, ii, 905).—In the case of the radium ...ive deposit, some 5 to 10% is deposited on the anode, and this ...been further investigated.   This part is ascribed to the ...tion of unchanged particles of radium-A, and no negatively ...rged particles exist.   F. S.

Origin of the Electron Emission from Glowing Sali
FRANK HORTON (*Phil. Trans.*, 1914. [*A*] **214**, 277—294) — Experiments
on the electron emission from Nernst filaments have been m
with the object of throwing further light on the origin of the
emissive effect and of testing the "chemical action" theory of the
working of an oxide electrode. A comparison was made of the
electron emission from a filament (1) when heated by a current
and by alternating currents; (2) when heated by the same
current and heated without conducting the heating
(3) heated in the ordinary manner and compared with that
of the same material when heated on platinum. These experi-
ments indicate that the electron emission is not connected
directly or indirectly with the electrolysis which accompanies
passage of the current. At a given temperature, the emission is
the same whether the current through the filament is great or
small. From this it may be inferred that the action of the
cathode is not due to the recombination of electrolytic products
calcium and oxygen, as has been suggested.

No definite conclusion can be drawn from the results as
to whether the electron emission is purely a thermal effect or
due in some way to chemical action. The fact that the emission
increases when a chemically active gas is allowed to enter the
charge tube may or may not be due to chemical action. It is
probable that the cause of the increased activity is not the same in
different cases. H. M. D.

Radium : Uranium Ratio in Carnotites. S. C. LIND and
C. F. WHITTEMORE (*J. Amer. Chem. Soc.*, 1914, **36**, 2066—2082). —
The samples of carnotite used in this investigation were representa-
tive of the principal occurrences in Colorado and Utah, and
containing from 1.5% to 33% of U_3O_8 were included. Samples
representing large quantities of ore (from a few hundred to
several tons) gave a ratio Ra : U identical with that of pitch-
blende, 3.33×10^{-7}. Samples from small quantities of ore
exhibited abnormal ratios, ranging from 2.48×10^{-7} to higher.
These abnormal ratios are probably due to a transport of
radium within a bed of ore, producing local differences which are
neutralised when large quantities of ore are mixed.

Carnotite has a high emanating power, varying from bed to bed.
In order to obtain concordant results by Boltwood's emanation
method, it was found desirable to make the determination of the
emanating power and the emanation liberated by solution act
complementary to each other by determining the emanation liber-
ated by solution on the same sample from which the emanating
power had just been determined. Radium can be more easily
determined by the emanation method in one operation, either in
solution or by ignition from tubes in which it has been sealed a
month to attain equilibrium. E. G.

The Electrical Resistance and Critical Ranges of Pure
Iron. G. K. BURGESS and I. N. KELLBERG (*J. Washington Acad.*,
1914, **4**, 436—440). —The variation of the resistance of pure

temperature has been examined between 0° and 950°. The method employed consisted in comparing the resistances of iron and platinum wires, which were wound on the same support and placed in an exhausted quartz tube heated in an electric furnace. With the aid of a drum-chronograph, the times at which the resistances were measured could be accurately recorded, the resistance of platinum wire affording a measure of the temperature of the iron wire at any moment.

The results show that the resistance of iron increases at a gradually increasing rate until the neighbourhood of the first critical region (A_1) is reached. This region is characterised by a point of inflexion on the resistance temperature curve at 757°. As the temperature is further increased, there is an abrupt fall in the resistance at about 894°, and the reverse change occurs at approximately the same temperature when the temperature is allowed to fall. This second critical region (A_2) extends over an interval of 5°. Whilst the change A_2 is reversible and does not appear to be associated with any alteration in crystalline structure, the change A_1 seems to be progressive and (thermo-electrically) non-reversible, and furthermore it is associated with a change in crystalline form.

H. M. D.

Measurement of Oxidation Potentials at Mercury Electrodes. I. The Stannic-Stannous Potential. GEORGE SHANNON FORBES and EDWARD PAYSON BARTLETT (*J. Amer. Chem. Soc.*, 1914, **36**, 2030—2040).—The work of earlier observers on the stannic-stannous potential has not given concordant results, and the present investigation has therefore been carried out.

It has been found that mercury is superior to platinum for use in measuring oxidation potentials of low intensity as results are obtained more rapidly and are less liable to be vitiated by irregularities in surface energy of the electrode or by the presence of traces of oxygen.

The potentials of mixtures of stannic and stannous chlorides containing ½ gram-atom of tin per litre in hydrochloric acid of three different concentrations have been measured at mercury electrodes at 25°. Some measurements were also made of mixtures containing ¼ gram-atom of tin per litre. The potential has been found to be nearly independent of the concentration, but is very slightly more electro-negative in the more dilute solutions.

In order to ascertain the values which should be observed if acid could be eliminated without the appearance of hydrolysis, the potentials for selected values of the concentration ratio have been plotted against the several concentrations of acid employed and extrapolated to zero concentration of acid; the graphs thus obtained are nearly straight lines. Up to two gram-mols. of hydrochloric acid per litre the potentials are expressed accurately by the formula $= 0.426 + 0.030 \log Sn^{IV}/Sn^{II} - 0.011 \times$ concentration of hydrochloric acid, provided that sufficient acid is added to prevent hydrolysis.

E. G.

Diffusion and Membrane Potentials. E. B. R. P...
(Trans. Faraday Soc., 1914, **10**, 160—166).—The membrane poten...
has been determined when two solutions of sodium between
different concentrations, are separated by parchment.
electrodes are used. The potentials observed are considerably ...
than the ordinary diffusion potentials. The effect appears to ...
decrease the mobility of the anion as compared with that of ...
cation, but the membrane is never completely impermeat... ...
anion.   C. H ...

Studies on a New Kind of E.M.F. I. REINHARD BEUTNER
(J. Amer. Chem. Soc., 1914, **36**, 2040—2045).—The *E.M.F.*
galvanic cells composed of insoluble inorganic liquids and aqueous
solutions (A., 1913, ii. 469) is discussed, and it is shown that a
change of the *E.M.F.* of such systems must be due to the change
of potential difference located at the junction of the organic and
and the aqueous solution   The observations on cells containing
salicylaldehyde as a middle conductor afford an imitation of ...
electrode-like potential differences between certain liquid and
and aqueous solutions (Loeb and Beutner, A., 1912, ii. 602.) It is
shown that the potential difference at the junction of the two
phases does not depend on ionic mobility as does the potential
difference between miscible solutions, but must have properties
characteristic of potentials at metallic electrodes.   E. G.

**Studies on a New Kind of E.M.F. II. Cell Arrangement
of Aqueous and Nitrobenzene Solutions Containing One
Common Ion in Both Phases.** REINHARD BEUTNER *(J. Amer.
Chem. Soc.*, 1914, **36**, 2045—2059).—In the preceding paper, reference
has been made to the existence of interphase potential differences
with properties resembling electrode potentials.

The *E.M.F.* of cells consisting of aqueous and nitrobenzene solu-
tions has now been measured. The solutions in contact with each
other always contain one common ion, and the potential difference
at the nitrobenzene water interphase can therefore be easily calcu-
lated from the thermodynamic formula. It is proved that the
E.M.F. of cells which consist of two nitrobenzene solutions in
contact with each other between two identical aqueous solutions is
located at the phase junctions, and not at the junction of the two
nitrobenzene solutions.

Ostwald has suggested that a selective ionic permeability of
membranes is the cause of physiological currents. According to this
hypothesis, the *E.M.F.* produced by a water-immiscible layer is not
located at the phase-junction but inside the layer or membrane.
This theory does not accord with the experimental results obtained
in the present investigation.   E. G.

Passivity of Metals. HORACE G. BYERS and SETH C. LANGE
(J. Amer. Chem. Soc., 1914, **36**, 2004—2011).—It has been shown in
earlier work (Byers, A., 1908, ii, 1026; Byers and Darrin, A., 1910,
ii, 579; Byers and Morgan, A., 1911, ii, 1057; Byers and Landi...

1913. ii. 552) that the establishment of the passive state in iron as an anode is affected by the character and condition of the of the electrolyte, the temperature, the current density, the mode of passage of the current, and the character of movement of the electrolyte. Experiments are now described which indicate another factor must be added to these, namely, the concentration of the dissolved oxygen about the anode, and that this is apparently the determining factor. When all these factors are taken into account, constant results can be obtained with respect to the time required to render iron passive with a given current in nitric acid, and a critical current density in nitric acid can be obtained.

Passivity, when not caused by a visible film of oxygen, is considered to be due to the fact that the rate of ionisation of certain metals is not sufficient to carry a current of more than a certain density. When such current density is exceeded, oxygen electrodes, consisting of occluded oxygen, are formed in electrolytes consisting of oxygen compounds. Non-anodic passivity is also regarded as due to occlusion of oxygen and consequent protection of the metal from attack.   E. G.

Electro-deposition of Cadmium. I. and II. FRANK C. MATHERS and HUGH M. MARBLE (Trans. Amer. Electrochem. Soc., 1914, 25, 315, 319 333).—I. A review of the work done in the refining and commercial plating of cadmium. Reference is made to work done with (1) sulphate solutions, (2) nitrate solutions, (3) haloid solutions, (4) silicofluoride solutions, (5) cyanide solutions, (6) phosphate solutions, (7) ammoniacal solutions, (8) oxalate solutions, acetate, formate, lactate, and succinate solutions, and (10) tartrate solutions.

II. A large number of experiments have been carried out with the object of determining which salts of cadmium are best suited to giving smooth, adherent, and non-crystalline deposits. Baths were made up of various cadmium salts containing 4% of cadmium, and electrolysed between cadmium electrodes with a cathode current density of 0·4 amp. per 100 sq. cm.; the solutions were stirred at intervals The deposits obtained from ammoniacal and alkaline nitrate baths were hopelessly spongy. The deposits from solutions of the bromide, iodide, sulphate, phosphate, and chloride were rough and crystalline. A number of experiments are described with chloride baths to which various other substances had been added, for example, a bath containing 4% of cadmium as chloride, 10% of sodium chloride, 5% of hydrochloric acid, and 0·1% of peptone gave a fairly smooth, finely crystalline deposit. A bath of the same composition as the foregoing with the addition of 10% of ferric chloride gave a much better deposit. Manganese, aluminium or calcium chlorides did not improve the deposit in the same way that iron did. The deposits obtained with solutions of bromide and iodide were crystalline and rough. Solutions of fluoride, silicofluoride, borofluoride, and perchlorate containing 4% of cadmium and 0·5—5·0% of the free acid and 0·2 gram of peptone, glue, or

phloridzin or 4 drops of oil of cloves gave excellent deposits, times in these cases spongy places, rough projections, and spots formed, but these are attributed to the presence of particles anode slimes, since they were not formed when the anode amalgamated. It is shown that the same substances, oil of cloves, glue, peptone, and phloridzin, which have been previously used to give quite good deposits in the case of lead, also produced deposits in the case of cadmium, although it was generally more difficult to obtain good deposits with cadmium than lead.   J. F.

A Thermo-regulator for Thermostats at Temperatures Very Close to Room Temperature. CHARLES W. R. Power (*J. Soc. Chem. Ind.*, 1914, **33**, 899—900).—A regulator is described for use with thermostats at temperatures either a few degrees below or above atmospheric temperature. The regulator consists of the usual toluene-filled vessel, which is fitted at the top with two tubes at different levels; the top one leads into the thermostat, the lower one into the sink, and both serve to conduct a stream of ice-cold water. The top of the regulator is closed by a cork, which carries a glass tube, by means of which ice-cold water enters the regulator, and a copper wire which terminates at the upper end the capillary of the regulator. A second wire is fused into the regulator in such a position that it is always in contact with the mercury column. These two wires are connected through an accumulator with a small electro-magnet. The magnet when energised operates a lever which deflects the flow of ice-cold water from the sink into the thermostat, and at the same time breaks the circuit of the electrical heater, so that the temperature is regulated very quickly. Using such an instrument, the author was able to maintain a temperature of 27° within ±0·5° in a 3-litre thermostat with the atmospheric temperature at 30°.   J. F.

Capacity for Heat of Metals at Low Temperatures. E. H. GRIFFITHS and EZER GRIFFITHS (*Phil. Trans.*, 1914, [A], 214, 319—357). The specific heats of a large number of substances have been measured at the ordinary temperature, and also at liquid air and liquid hydrogen temperatures, but there have been as yet no sure measurements of the true specific heats at intermediate temperatures. In order to bridge the gap, the authors have worked a method for maintaining the temperature of an enclosure constant at any point between that of the room and −165° by a judicious application of the Joule-Thomson effect. The method employed for the measurement of the specific heats of metals depends on the determination of the rise in temperature of a block of the metal which is suspended in the constant temperature enclosure and supplied with a measured quantity of electrical energy.

Experiments were made at various temperatures within the above-mentioned range on aluminium, copper, zinc, silver, cadmium, lead, iron, and sodium. Atomic heat temperature curves have been constructed from these data in combination with the results obtained by Nernst at liquid air and hydrogen temperatures

... comparing the experimental curves with the requirements of the formulæ put forward by Einstein (*Ann. Physik*, 1907, [iv], 22), Nernst and Lindemann (A., 1911, ii, 466), and by Debye (1912, ii, 1134), it is found that none of these formulæ is capable of representing the results over the entire temperature range. Debye's formula appears to give the nearest approximation for the lowest portion of the range, but systematic divergences occur at the higher temperatures. This may be due either to the assumptions made by Debye being valid only at very low temperatures, or it may mean that heat energy, additional to that involved in the three degrees of freedom ascribed to the atom, must be taken into account. Above liquid air temperatures the three formulæ are capable of representing the results approximately, but in some cases the discrepancies are considerable.

H. M. D.

Metastability of the Metals in Consequence of Allotropy and its Significance for Chemistry, Physics and Technics. ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 203. Compare this vol., ii, 202).—A review of the earlier literature dealing with the specific heat of the metals affords evidence that the specific heat depends in many cases on the previous history of the metals. For copper, zinc, lead, aluminium, etc., the specific heat temperature curve is not continuous, but varies abruptly at one or more points. This behaviour is in agreement with dilatometric observations, which indicate the existence of two or more modifications of some of these metals. H. M. D.

Determination of the Freezing Point for Salt Solutions. H. VAN DER LAAN (*Chem. Weekblad*, 1914, **11**, 925—927).—In measuring the freezing point of a salt solution, homogeneity of the liquid must be ensured by vigorous agitation. Failure to observe this precaution leads to inaccurate readings for such solutions, but is immaterial for such liquids as water or milk. A. J. W.

Boiling Points in Homologous Series. S. SUGDEN (*Chem. Soc.*, 1914, **110**, 152—153, 165—168).—It is found that the boiling points of the members of homologous series of carbon compounds can be satisfactorily represented by means of the formula $M \cdot b = \sqrt{M} + aM/b$, in which M is the molecular weight, b the boiling point, and a and b are constants. The formula is found to be applicable to the paraffins, alkyl haloids, aldehydes, acids, amines, alkyl cyanides, normal primary and secondary hydrosulphides, esters, nitroparaffins, ethers, olefines, and aromatic hydrocarbons. The average difference between the found and calculated boiling points for some one hundred and fifty compounds is 1·63°. The values of a vary to a comparatively small extent from one series to another, the aromatic hydrocarbons having the highest value (45·71) and the olefines the lowest value. The values of b vary to a much larger extent, the extremes being given by the alkyl iodides ($-2038·0$) and the nitroparaffins (...).

H. M. D.

Vapour Pressures of Silver, Gold, and Bismuth Ama... ERMON DWIGHT EASTMAN and JOEL H. HILDEBRAND (*J. Amer.* *Soc.*, 1914, **36**, 2020—2030).—In continuation of a study of the of concentrated solutions from the point of view of ... tions (Hildebrand, A., 1913, ii, 755), measurements ... made of the vapour pressures of silver, gold, and bismuth ... at about 318° by the method used in the case of the ... (*loc. cit.*).

As silver is but sparingly soluble in mercury at ... determination was made, namely, with an amalgam ... 1·27% of silver. In this case Raoult's law was obeyed ... limits of experimental error.

Measurements with gold amalgams, at concentrations ... 23·7% of gold, showed the separation of a solid phase ... 16·5% concentration. In the more dilute amalgams the ... pressures were greater than those calculated from Raoult's ...

Bismuth amalgams of all concentrations are liquid at ... also give higher vapour pressures than those calculated ... Raoult's law.

For the gold and bismuth amalgams, equations ... derived by Laar (A., 1910, ii, 583; 1913, ii, 670), are ... satisfactorily express the values observed.   E. ...

Method of Finding the Partial from the Total Vapour Pressures of Binary Mixtures, and a Theory of Fractional Distillation. M. A. ROSANOFF, C. W. BACON, and JOHN ... SCHULZE (*J. Amer. Chem. Soc.*, 1914, **36**, 1993—2004).—Rosa... Bacon, and White (this vol., ii, 766) have described a simple ... of measuring the partial vapour pressures of liquid binary ... which consists in distilling the mixtures and analysing succes... secutive fractions. In some cases the analysis cannot be so ... accomplished, and the experimental determination of the par... pressures would therefore be untrustworthy.

It is now shown that the partial pressures can be calculated ... the total vapour pressure by means of the general relation :

$$d\pi/dx = [(P_1 - P_2)/(\log P_1 - \log P_2)] \log [p_1(1 - x)/p...]$$

where x is the molar fraction of one of the components ... liquid, π the total pressure, p_1 and p_2 the partial pressures, ... and P_2 the vapour pressures of the isolated compounds. Cal... tions have been made by means of this expression for mixtures carbon tetrachloride and benzene, ethyl iodide and ethyl ... chloroform and acetone, and benzene and toluene, and the ... agree satisfactorily with those obtained experimentally.

A theory of fractional distillation is presented for the ... which the vapour escapes from the still without having under... any reflux condensation. This theory is based solely on the ... ciples involved in the equation given in the preceding para...
                                                                        E. ...

Measurements of Isotherms of Hydrogen at 20° and 15 PH. KOHNSTAMM and K. W. WALSTRA (*Proc. K. Akad. Wet.* *Amsterdam*, 1914, **17**, 203—216).—The authors have investi...

...compressibility of hydrogen at 15·5° and 20° for pressures ...ing from about 200 to about 2300 atmospheres. The lower ...perature was chosen in order to enable a comparison to be made ...he results with those obtained by Amagat.

...preliminary experiments with air, it was found that at high ...res the mercury quickly became contaminated, in consequence ...he formation of mercuric oxide. This prevented the carrying ...of measurements on the pressure-volume relations of air and ...

H. M. D.

...he Hydrogen Isotherms of 20° and 15·5° between 1 and ...0 Atmospheres. K. W. WALSTRA (*Proc. K. Akad. Wetensch.* ...erdam, 1914, 17, 217—224. Compare preceding abstract). The ...herms at 20° have been compared with those of Schalkwyk, ...hose at 15·5° with the data given by Amagat. For this pur-...al equation of the form $PV = a + bD + cD^2 + dD^4 + eD^6$, in ...h D is the density and a, b, c, d, e are coefficients. In so far ...comparison is possible, the author's observations appear to be ...atisfactory agreement with Schalkwyk's. Between 700 and ... atmospheres, the values of PV given by the author's results ...somewhat greater than those calculated from Amagat's data, ...he difference is particularly marked for pressures above 2000 ...spheres.

H. M. D.

...Isothermals of Monatomic Substances and their Binary ...tures XVI. New Determination of the Vapour ...sures of Solid Argon down to −205°. C. A. CROMMELIN ...*K. Akad. Wetensch. Amsterdam*, 1914, 17, 275—277. Compare ... c. 181—The vapour pressures of solid argon have been ...mined over the temperature interval −189·64° to −205·32°. ...ressures corresponding with these limiting temperatures are ...ely 49·78 and 3·830 cm. of mercury. The experimental ...ults are compared with the values calculated according to ...mulæ of Rankine and Bose, Nernst and Sackur. Sackur's ...which is based on Nernst's heat theorem, affords satisfac-...agreement at the higher temperatures, but there are wide ...ces at the lower.

... heat of sublimation of solid argon, calculated from the ...perature variation of the vapour pressure, falls from 47·36 at ...·64° to 44·51 at −205·32°.

H. M. D.

...New Relation between the Critical Quantities and the ...our of All Substances in their Thermic Behaviour. J. J. ...AARS (*Proc. K. Akud. Wetensch. Amsterdam*, 1914, 17, 451—465. ...pare this vol., ii, 341).—A theoretical paper in which the author ...es at the conclusion that the quantity a in the van der Waals' ...tion is independent of the density over a very large range. ... molecular attraction in both the gaseous and liquid states is ...re satisfactorily represented by a/v^2. Whether a is also ...pendent of the temperature cannot as yet be determined with

... XVI. ii.

perfect certainty. With reference to the quantity b [illegible]
tion, the evidence is distinctly in favour of its depe[illegible]
density and temperature. The significance to be atta[illegible]
that of the volume (m) occupied by the molecules, and [illegible]
assumption that $b = 4m$ must be discarded.

The thermal behaviour of a substance is not only depe[illegible]
the quantities a and b, which determine the critica[illegible]
but also on the absolute value of the temperature at [illegible]
substance is considered. Every substance passes from [illegible]
type to the ideal type when the temperature falls [illegible]
and approximates to absolute zero.   H. M.

Free Energy of Oxygen, Hydrogen, and the Ox[illegible]
Hydrogen. GILBERT N. LEWIS and MERLE RANDALL (J. Amer[illegible]
Soc., 1914, 36, 1969—1993).—In an earlier paper (Lewis, A.
ii, 112) an account was given of the general methods used
energy calculations. These methods have now been appli[illegible]
determination of the free energy of oxygen, hydrogen[illegible]
hydrogen oxides. The calculations have been made [illegible]
existing data, but in some cases data have been employ[illegible]
were obtained in the course of investigations not yet pub[illegible]

The following are the values (in calories) of the free [illegible]
formation (F^o 298) from the elements in their standard [illegible]
ozone (O_3), 32,400; hydrogen (H), 30·550; hydrogen ion H
hydroxyl ion (OH′), −37·385; water (liquid), 56·6[illegible]
(gas), −54,567; water (solid), −56,478; hydrogen per[illegible]
aqueous solution), −30,970; hydroperoxide ion (HO₂) [illegible]
hydrogen peroxide (liquid), −27,770; hydrogen per[illegible]
−24,270.   ?

Combustion Calorimetry and the Heats of Combust[illegible]
Sucrose, Benzoic Acid, and Naphthalene. HOBART C. D[illegible]
(J. Washington Acad. Sci., 1914, 4, 434—435). A critical [illegible]
the stirred water calorimeter, as used for bomb comb[illegible]
been made, and it has been found that the chief sourc[illegible]
may be avoided by the use of a suitably designed calor[illegible]
with resistance thermometers. Determinations of the h[illegible]
bustion of naphthalene gave 9622±2 cal. per gram, w[illegible]
mum deviation from the mean of about 5 in 10,000 for [illegible]
observations on the same sample. The value obtained [illegible]
acid was 6329±1 cal. per gram, with a maximum deviat[illegible]
5 in 10,000, and for sucrose 3949±2 cal. per gram, w[illegible]
mum deviation of about 1 in 1000.

The results indicate that benzoic acid is the most suita[illegible]
three substances for calibration purposes. The volat[illegible]
naphthalene necessitates special precautions when this [illegible]
employed, and sucrose is less well adapted, not only [illegible]
of the lower precision of the results, but also because [illegible]
heat of combustion and its frequent failure to ignite.
                                                       H. M.

Flames with Ether. ALAN LEIGHTON (*J. Physical Chem.*, 18, 619—622).—Perkin (T., 1882, **41**, 363) showed that when was evaporated in a shallow dish on a hot sand bath, a pale flame was produced, only visible in the dark, which did not the ether. This phenomenon had been previously observed by Döbereiner, and others. The author has investigated this and shows that it may be produced in many ways, among may be noted the following. A copper ball is heated to redness, and then allowed to cool until it just becomes in-, it is then suspended over a dish containing layers of filter soaked in ether, when a tall, blue flame is produced. The is produced at temperatures below dull redness, but above It has a comparatively low temperature, and the fingers x placed in it with impunity. It is shown that the flame is and when ether vapour is mixed with a small amount of and no hot surface is necessary. It may therefore be pro- by mixing ether with a non-inflammable volatile liquid and the mixture to evaporate and lighting the mixture with or by mixing ether vapour with a non inflammable gas, carbon dioxide. Similar flames can be obtained by re- ether by carbon disulphide; all the flames have low That from carbon disulphide and carbon tetra- has a temperature of 90°.   J. F. S.

ory of Molecular Volumes. IV. GERVAISE LE BAS (*Phil.* , [vi]. **28**. 439—466. Compare this vol., ii, 173, 340, 539) influence of ring structure on the molecular volume has amined by reference to the data for a large number of containing one or more rings. The data in question the most part to homocyclic compounds, but heterocyclic are also considered.

relationships exhibited lead to the conclusion that molecular influenced by ring structure to an extent which depends number of rings and on the number of groups in the rings. in general is a contraction, which is contributed to by elements of the nucleus, and often by the atoms which are with these. The contraction is the same whether two rings are separated or condensed; from this it would seem common atoms of the two or three rings must have extra- small volumes.

actions characteristic of the various polymethylene given as: *cyclo*propane, - 5·3; *cyclo*butane, -8·6; *cyclo*- -12·3; *cyclo*hexane, -16·1; *cyclo*heptane, -20·16; , -24·0. The corresponding value for the benzene ring

action attributed to the influence of atoms or groups in ation with the elements of the ring nucleus is supposed characteristic of atoms or groups which possess residual this residual affinity is neutralised, the contraction, as appears. The following values are given for the contrac- due to the different groups in combination with the

C_6H_5 nucleus: OH, -1.5; CN, -1.6; CH_2Cl, -1.9, P⟨⟩
NO_2, -2.7; COCl, -1.8; NH_2, -4.4; CO_2H, -2.8 ⟨⟩ ⟨
particular effect is described as the volume anomaly ⟨⟩   H. M.

The Unit-Stere Theory of Molecular Volume. Easterfield
stone *(Phil. Mag.*, 1914, [vi], **28**, 600—606).—A criticism of
unit-stere theory advanced by Le Bas (A., 1907, ii, 774).
ratio V/W, where V is the molecular volume and W ⟨⟩
the valencies, may be considered as the product of the
volume v and M/W, where M is the molecular weight of
member of a homologous series of compounds, M/W ⟨⟩
quantity $(a+n.14)/(a'+n.6)$, where a represents the
weight of the first member of the series, n the number
groups, and a' the sum of the valencies for the first member
the higher members of such a series M/W becomes practically
stant and equal to $14/6$ or 2.33. Since v also tends to a con-
stancy, the observed constancy of V/W in the higher members
homologous series can be readily explained. In so far as the
members of such series are concerned, the observed variation
V/W can be explained by the relative variations in the ⟨⟩
v and M/W.   H. M.

The Unit-Stere Theory. GERVAISE LE BAS *(Phil. Mag.*,
[vi], **28**, 607—608).—A reply to Vanstone's criticism, ⟨
preceding abstract). The author considers that the ⟨⟩
volume is not divisible into factors represented by the ⟨
volume and the ratio of the molecular weight to the sum
valencies.   H. M.

Existence of Compounds in Binary Liquid Mix
J. HOWARD MATHEWS and RAYMOND D. COOKE *(J. Physics*,
1914, **18**, 559—585).—Starting from the expression of
Batschinski (A., 1913, ii, 928), the authors show that the is
specific volume curves of non-associated liquids are straight
whereas those of associated liquids are concave toward the
axis. The authors show that further evidence of the exist
compounds in certain liquid mixtures is obtained by the
fluidity–specific volume isotherms of binary mixtures, and that
that this evidence supports the view that a maximum in
viscosity composition curve of a binary mixture is due to
the presence of a compound. Twenty-four pairs of liquids
plotted in this manner, and of these nine exhibit maxima
the other fifteen give straight lines. The values used in the
are taken from the work of Dunstan (T., 1904, **85**, ⟨⟩
and Rodger (T., 1897, **71**, 360), Linebarger, Faust, and
New determinations have been made of the pairs acetic acid–
(56—44%), methyl alcohol–water (36—64%), propyl alcohol–
(50—50%), water–acetic acid (22—78%), water–pyridine (5
acetic acid–pyridine (77—23%), ethyl alcohol–water (5
chloral–water (88—12%), and chloral–ethyl alcohol (44%
The measurements were made at temperatures from 0° to ⟨

...all bibliography of the work done on viscosity, as far as it ... to the chemical and molecular constitution and on the ...ties of completely miscible liquids, is appended to the paper.

J. F. S.

...mperature-coefficients of the Free Surface Energy of ...yds at Temperatures from −80° to 1650°. I. Methods ...Apparatus. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam,* 17, 329–365).—An arrangement of apparatus is described by ... of which it has been found possible to make accurate ...rements of the surface tension of liquids at temperatures ... −80° and 1650°. A capillary tube, provided with a ... knife-edge opening, is immersed in the liquid perpendicular ... surface, and a small bubble of gas is allowed to form slowly ... end of the capillary tube. The pressure in the gas bubble ... moment when the bubble is about to burst affords a measure ... surface tension of the liquid. Provided that abnormally ...iscosities are not encountered, the author considers that the ... obtained with his apparatus are as accurate at 1650° as at ...nary temperature.

... results obtained at different temperatures for a number of ... substances and for several inorganic salts are recorded in ... A comparison was also made between the surface tensions ... water and colloidal solutions of ferric hydroxide and silicic ... The curves showing the relation between the surface-energy ... temperature are of the same kind, but those for the ... solutions are situated above the curve for water.

H. M. D.

...perature-coefficients of the Free Surface Energy ...iquids at Temperatures from −80° to 1650°. II. ...rements of Some Aliphatic Derivatives. F. M. JAEGER ...d J. SMIT (*Proc. K. Akad. Wetensch. Amsterdam,* 1914, ... 353).—Measurements of the temperature variation of the ... surface energy (*μ*) have been made for *n*-propyl alcohol, ...l alcohol, diethyl ether, ethyl formate, ethyl chloro-formate, ...etate, methyl *iso*butyrate, ethyl *iso*butyrate, *iso*butyl *iso*-...e, acetone, methyl propyl ketone, ethyl acetoacetate, methyl ...toacetate, ethyl propylacetoacetate, methyl, ethyl, ...butyl, *iso*butyl and amyl cyanoacetates, chloroform, carbon ...ide, and *iso*butyl bromide. In most cases *dμ/dt* decreases ... of temperature. Where an increase was observed this ... traced to decomposition of the substance. H. M. D.

...perature-coefficients of the Free Surface Energy of ...s at Temperatures from −80° to 1650°. III. Measure-...of some Aromatic Derivatives. F. M. JAEGER and M. J. ...(*Proc. K. Akad. Wetensch. Amsterdam,* 1914, 17, 386—394). ...lowing substances were examined: nitrobenzene, *o*-nitro-... aniline, dimethylaniline, *o*-toluidine, thymol, methyl, ...nd benzyl benzoates, salicylaldehyde, acetophenone, and

α-campholenic acid. The curves obtained by plotting the molecular surface energy against the temperature are concave to the axis in the case of nitrobenzene, o-nitrotoluene, aniline, and others, indicating that du/dt increases with the temperature. In their behaviour these substances resemble water, but differ from the majority of the substances examined in the previous paper (preceding abstract).   H. M.

Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from – 80° to 1650°. IV. Measurements of Some Aliphatic and Aromatic Esters. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam,* 1914, **17**, 395—405).—The data recorded refer to amyl acetate, ethyl and ethyl malonate, ethyl bromomalonate, ethyl benzylethyl, methyl and ethyl tartrates, methyl, ethyl and phenyl salicylate, methyl cinnamate, and o-nitroanisole. The surface-energy-temperature curves indicate a sharp rise in du/dt when the temperature is sufficiently high for decomposition to take place.   H. M.

Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from – 80° to 1650°. V. Measurements of Homologous Aromatic Hydrocarbons and Some of their Halogen Derivatives. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam,* 1914, **17**, 405—415).—Data are given for benzene, toluene, *p*-xylene, mesitylene, ψ-cumene, cumene, phenylmethane, chlorobenzene, bromobenzene, *m*-dichlorobenzene, *p*-bromofluorobenzene, *m*-fluorotoluene, and *p*-chlorotoluene. The hydrocarbons and their halogen derivatives afford examples of an increase and decrease in the value of du/dt with rise of temperature. The deviations of the surface energy-temperature curves from straight lines are so large in many cases that they cannot be accounted for by error of experiment. In the case of xylene, for instance, du/dt increases from 1·60 for the interval 42° to 3·0 for the interval 146° to 166°.   H. M.

Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from – 80° to 1650°. VI. General Remarks. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam,* 1914, **17**, 416—430). Compare preceding abstracts. From collected results recorded in the previous papers it would seem that the temperature-coefficient of the molecular surface energy is independent of the temperature, or with rise of temperature may increase or diminish. No connexion can be traced between the class to which a particular liquid belongs and the magnitude of its molecular surface energy, or of its temperature-coefficient. The absence in general of a linear connexion between the surface energy and the temperature is supposed to be connected with the value of surface energy, and this departure from linearity is to be expected whenever the interval of temperature examined is wide enough.

With regard to the connexion between the molecular surface

energy and the chemical nature of the liquid, it is found that the surface energy at the same temperature increases in homologous series with the molecular weight. Replacement of hydrogen by alkyl, by the nitro- or amino-groups, and by aromatic hydrocarbon radicles leads to an increase in the molecular surface energy when the comparison is made at a fixed temperature. H. M. D.

The **Adsorption of Vapours.** A. M. WILLIAMS (*Trans. Faraday Soc.*, 1914, **10**, 167—171. Compare this vol., ii, 111).— Adsorption near to the saturated vapour pressure of a liquid is large and independent of the temperature, but is not necessarily maximum. C. H. D.

"**Negative" Adsorption.** A. M. WILLIAMS (*Trans. Faraday Soc.*, 1914, **10**, 155—159. Compare this vol., ii, 111). —The adsorption of cæsium chloride and magnesium sulphate by charcoal increases with the concentration to a maximum, decreases, passes through zero and becomes negative. Ammonium chloride also exhibits a minimum. C. H. D.

Action between Clay Filters and Certain Salt Solutions. B. HICKS (*J. Ind. Eng. Chem.*, 1914, **6**, 829—831).—Filtration through porcelain clay filters produces little or no change in the acid content of $N/10$-borate solutions, a slight decrease, about 1% in concentration in $N/10$-alkali chloride and sulphate solutions, a larger decrease in $N/10$-alkali carbonate solutions, and a still larger decrease, 8%, in the case of $N/1000$-alkali carbonate solutions. Ammonia and potassium are also absorbed by the filters from solutions of their salts; the retained ammonia may be removed by washing the filter with potassium chloride solution, but in the case of potassium a small quantity is persistently retained by the filter even after persistent washing with water and ammonium chloride solution. W. P. S.

The Theory of Colloid Chemistry. WILDER D. BANCROFT (*J. Physical Chem.*, 1914, **18**, 549—558).—A lecture delivered to the general meeting of the American Chemical Society, in which a new theory of colloid chemistry is discussed. The theory is based on the four postulates: (1) Colloid chemistry differs from ordinary chemistry only through the variations resulting from the increasing dispersity of one or more phases. (2) Selective adsorption occurs at surfaces. (3) Sufficiently finely divided particles, if are prevented from coalescing, will be kept suspended in a solution by the Brownian movements; and (4) under fixed conditions of peptonisation an approximately definite limiting concentration is obtained corresponding with a saturated solution in the case of a true solution. J. F. S.

Equilibria in Ternary Systems. XVI. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 169—182. Compare this vol., ii, 634).—A further discussion of the equilibrium relation-

ships for the case in which one of the three components is specifically non-volatile.

H. M. D.

New Form of Intermittent Siphon. W. A. BRADLEY (*Chem. News*, 1914, **110**, 163).—A simple form of intermittent siphon described, which permits of the automatic flushing of the liquid in a gas absorption tube with a small quantity of liquid. The siphon is used in conjunction with a constant feed of water, and the capacity of the flush can be varied by a simple adjustment.

H. M. D.

Inorganic Chemistry.

Displacement of Acids by Hydrogen Peroxide.
JOACHIM SPERBER (*Chem. Zentr.*, 1914, i, 2139; from *Schweiz. Apoth. Zeit.*, 1914, **52**, 245—248. Compare this vol., ii, 557. The action of hydrogen peroxide on halogen acids has been further studied. The affinity of the halogen hydrides for hydrogen peroxide varies as the affinity of the halogen for oxygen, hydrogen iodide is most easily decomposed. The reaction depends on the order in which the substances are brought together. When hydrogen iodide is added to hydrogen peroxide, the reaction is so violent that the iodine which is first liberated volatilises, leaving a colourless liquid; but when hydrogen peroxide is added to an excess of the acid, although the reaction is vigorous, the iodine does not disappear. Exactly the reverse is the case with the other acids. The reaction is more energetic when hydrogen peroxide is added to the acid. The acid salts behave in the same way, from which it appears that hydrogen peroxide first liberates the free acid and then decomposes it. This view is supported by the fact that ammonium peroxide (D'Ans and Wedig, A., 1913, ii, 1051) precipitates the peroxides from solutions of the alkaline earth haloids.

J. C. P.

The System Ammonia-Water. A. SMITS and S. Postma (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 182—194).—Exact cooling-curve observations have enabled the authors to give a more complete description of the freezing-point diagram. The two compounds $2NH_3,H_2O$ and NH_3,H_2O melt at $-78\cdot9°$ and $79\cdot5°$ respectively. The eutectic point at which ammonia and $2NH_3,H_2O$ exist as solid phases lies at $81\cdot4$ mols. % of ammonia and $-92\cdot5°$; the point at which $2NH_3,H_2O$ and NH_3,H_2O co-exist lies at $57\cdot5$ ammonia and $-86\cdot0°$, and that corresponding with the co-existence of NH_3,H_2O and ice at $34\cdot7\%$ of ammonia and $-100\cdot3°$. Except in the interval for mixtures containing 30—40 mols. % of ammonia the authors' data agree satisfactorily with those of Rupert (A., 1909, ii, 726; 1910, ii, 605).

The vapour pressures of binary mixtures of varying composition have also been determined over a considerable interval of temperature, but the curves constructed on the basis of these data afford no trace of the formation of definite compounds.   H. M. D.

Action of the Silent Electric Discharge on Mixtures of Hydrogen and Nitrogen. M. LE BLANC (*Chem. Zentr.*, 1914, ii, 1 ; from *Ber. K. Sächs. Ges. Wiss., Math.-phys. Kl.*, 1914, **66**, 651).—Earlier experiments (Le Blanc and Davies, A., 1908, ii, 1 ; Davies, A., 1909, ii, 30) indicated that the formation of ammonia by the silent electric discharge does not obey the law of mass action. This might have been due to alterations in the electrical conditions, caused by changes in the composition of the gaseous mixture. It is now found, however, that, even when the gases are largely diluted with a helium–neon mixture, the quantitative results are the same. The old experiments have been repeated ; better apparatus, and the phenomena are found to be very complicated. The amount of ammonia formed depends on the dimensions of the apparatus, and the density and oscillation frequency of the current.   J. C. W.

Volatilisation of Arsenious Acid from Aqueous Solutions containing Hydrochloric Acid. BERTRAM JAMES SMART and JAS T. PHILPOT (*J. Soc. Chem. Ind.*, 1914, **33**, 900—902).— Mixtures of 200 c.c. of hydrochloric acid solution of various concentrations, both above and below that of the constant boiling mixture, containing various quantities of arsenious acid, have been subjected to fractional distillation. The distillates have been analysed with the object of ascertaining to what extent and under what conditions the arsenic volatilises with the acid. It is shown that when solutions are distilled, those which contain the greatest concentration of hydrochloric acid give off the arsenic most rapidly. When hydrochloric acid is present to the extent of about 190 grams per litre or more, the concentration of arsenic in the solution being undistilled rapidly falls as the solution is fractionated. In solutions containing less than 180 grams of hydrochloric acid per litre, the concentration of arsenic in the solution remaining undistilled rises, although some of the arsenic passes over, the ratio between acid and arsenic remaining practically constant until the solution contains about 185 grams of hydrochloric acid per litre. This point corresponds approximately with a hydrate of the formula $HCl,8H_2O$. When the acid becomes more concentrated the proportion of arsenic volatilised increases rapidly.   J. F. S.

The Reduction of Arsenic Acid to Arsenious Acid by means of Thiosulphuric Acid. ROBERT M. CHAPIN (*Chem. Zentr.*, 1914, ii, 2032—2033 ; from *J. Agric. Res.*, 1914, **1**, 515—517). . . Arsenic acid is completely and quickly reduced to arsenious acid in the cold by a mixture of sodium thiosulphate and a mineral acid. The speed of the reaction depends to a great extent on the concentration of the hydrogen ions, and the course of the reduction is

influenced by the amounts of the reagents and by the ____
which they are mixed. The reaction is therefore _____
appears to correspond with the reduction of a dichromate __
sulphuric acid (compare Stiasny and Das, A., 1912, ii. ___

J. C. W

Isotherm of the Solubility of Lithium Chloride at 25 __
Mixtures of Water and Ethyl Alcohol. S. PiŠA __ ___
(*Anal. Fis. Quim.*, 1914, **12**, 343—349).—The solubility of __
chloride in aqueous alcohol decreases regularly in solvent ___
ing up to 70% by weight of alcohol; the solubility curve ___
linear, the coefficient being 0·6939 per gram of alcohol. The __
during this stage exists as LiCl,H₂O. The anhydrous ___
posited from solutions in pure alcohol.
G. [L. ?]

**Silicate Chemistry. II and III. Lithium Alum___
Silicates the Composition of which Corresponds** with __
of the Minerals Eucryptite and Spodumene. F. M. J___
and ANT. ŠIMEK (*Proc. K. Akad. Wetensch. Amsterdam*, i h ___
239—251, 251—270. Compare this vol., ii, 363). II A ___
aluminium silicate of the composition LiAlSiO₄ has been prep___
from a mixture of lithium carbonate, alumina, and silica by __
ing in a closed crucible at 1500°. When the fusion is ___
cooled, small, irregularly shaped crystals are obtained, for __
measurements of the mean refractive index and the density __
$n_D = 1·531$ and D = 2·362 at 25°. These data indicate ___
artificial silicate is not identical with the mineral eucry___
the synthetic product has been named *pseudo-eucryptite*. __
fusion is rapidly cooled by quenching, a pseudo-eucryptite __
obtained, for which $n_D = 1·541$. This glass is metastable __
gard to the birefringent crystalline modification, and is __
converted into this on heating at 900°. The melting p___
pseudo-eucryptite is given as 1388°.

The compound LiAl(SiO₃)₂ was prepared by fusion of ___
of the same substances containing a larger proportion of __
The purest product obtained was found to melt at 1400 __
$n_D = 1·521$ and D = 2·411 at 25°. Since the physical pr___
differ appreciably from those of the mineral spodumene __
synthetic product has been named *β-spodumene.*

III. For the purpose of comparing the properties __
synthetic β-spodumene with the mineral varieties, the au___
determined the melting points and densities of a num___
kunzites and spodumenes. The data indicate that, in gen___
melting points of the natural kunzites are considerably h___
the values obtained for the synthetic products. It was __
that the melting points of the minerals decrease as the de___
increase.

Micrographic examination of the products which are __
when the mineral varieties of lithium aluminium silicate are __
and allowed to cool slowly afford evidence that β-spodumene __
thereby formed. These observations lead to the conclus___

in natural kunzites, hiddenites, and spodumenes are metastable forms (α spodumenes) of the compound, and that β-spodumene the stable form at all temperatures below 1400°. The natural spodumenes cannot therefore be produced from dry magmas, and it is probable that their formation is due to so-called "hydrothermal" synthesis.

A lithium aluminate of the composition LiAlO₂ was prepared by fusion of a mixture of lithium carbonate and alumina at 900°, and then at 1200°. It forms microscopic hexagonal or octagonal plates which show pronounced double refraction. The indices were found to be $n_D = 1·604$ and $n'_D = 1·615$; $D^{\circ\circ} 2·554$. The melting point could not be determined, but it is higher than 1625°.

H. M. D.

Cæsium Alum and Its Properties. EDWARD HART and HARRY B. HUSELTON (*J. Amer. Chem. Soc.*, 1914, **36**, 2082—2084).—The solubilities of cæsium alum, expressed as the number of grams of the anhydrous salt, AlCs(SO₄)₂, per 100 grams of water, have been determined as follows: at 7°, 0·26; at 19°, 0·42; at 22°, 0·43; at 24°, 0·47; at 29·5°, 0·57; at 31·5°, 0·60; at 40°, 0·86; at 41°, ..., at 47°, 1·17; at 49·25°, 1·39; at 50°, 1·42; at 56°, 1·86; at 60°, 2·06; at 66°, 2·85; at 68°, 3·13; at 80°, 5·78. Two determinations of the specific gravity of the hydrated alum gave a mean value 1·945. The crystals melt in their water of crystallisation at 117°. These values are compared with those recorded by other observers.

E. G.

Influence of Certain Hydroxylic Compounds on the Solubility of Mercuric Chloride in Water. E. MOLES and M. MARQUINA (*Anal. Fís. Quím.*, 1914, **12**, 383—393).—Glycerol and others increase the solubility of mercuric chloride in water, whereas tartaric and citric acids decrease it. The solubility in glycerol is 1 in 1·25 at 25° ± 0·02.

G. D. L.

Terbium. C. JAMES and D. W. BISSEL (*J. Amer. Chem. Soc.*, 1914, **36**, 2060—2066).—Urbain (A., 1909, ii. 671) has stated that terbium is homogeneous, whereas Welsbach (*Chem. Zeit.*, 1911, **35**, 658) has expressed the opinion that it consists of three different elements. The present paper gives an account of a further study of this question.

The material employed consisted of gadolinium oxide containing terbium oxide, together with dysprosium and holmium oxides and traces of yttrium and erbium. It was converted into the bromates, which were submitted to a long and careful fractionation. The results indicate that terbium is a single homogeneous element. The bromate process effects a comparatively rapid separation of terbium from gadolinium; neodymium, if present, comes between these metals.

E. G.

The Acidic and Colloidal Characteristics of Aluminium Hydroxide. R. E. SLADE and W. G. POLACK (*Trans. Faraday Soc.*, 1914, **10**, 150—154).—Mahin, Ingraham and Stewart (A., 1913, ii,

139) stated that a solution of sodium aluminate is really a colloidal solution of the hydroxide in the alkali. It is now shown that the conclusions which these authors drew from their experiments in support of the above view, were unjustified. Conductivity measurements of such solutions are against the assumption of colloidal particles, and, when hydrolysis takes place, crystalline aluminium hydroxide is deposited. The ultramicroscope affords no conclusive evidence either way.   J C W

Advances in the Metallurgy of Iron and Steel. Sir Robert HADFIELD (*Trans. Faraday Soc.*, 1914, 10, 1—43.—A lecture delivered to the Faraday Society on June 11th, 1914.   C H D

Chromyl Chloride. II. E. MOLES and L. GÓMEZ (*Anal. Fis. Quim.*, 1914, 12, 142—154. Compare A., 1912, ii, 560).   Analyses of recently prepared chromyl chloride give values very close to the theoretical, and lead to the supposition that the earlier work probably did not examine the pure compound. No change was observed after two months, but after nineteen months a little coloured solid was deposited, which is possibly a polymeride.

The heat of solution was found to be 17·86 cal. (Berthelot, 17.7

The molecular weight, determined cryoscopically in carbon tetrachloride, tin tetrabromide, and antimony pentachloride, points to the formation of molecular complexes in conformity with the tendency to polymerisation noted above.   G D L

Inorganic Solvents. I. Antimony Pentachloride. E. MOLES (*Anal. Fis. Quim.*, 1914, 12, 314—343).—Pure antimony pentachloride is lemon-yellow in colour, acquiring an orange tint by the presence of chlorine. It has m. p. 3·0°, cryoscopic constant 18·5, heat of fusion 8·17 cal., and D⁴ 2·3356.

The action of antimony pentachloride on potassium iodide probably leads to the formation of iodine monochloride. Sulphur, selenium, and tellurium yield the crystalline double compounds of their tetrachlorides with antimony pentachloride.   G D L

Dilute Solutions of Aluminium in Gold. C. T. HEYCOCK and F. H. NEVILLE (*Phil. Trans.*, 1914, [A], 214, 267—276).—The equilibrium relations exhibited by aluminium and gold have been investigated by experiments on mixtures containing up to 5% weight of aluminium. The actual observations consisted in the tracing of cooling curves and in the microscopic examination of ingots which had been annealed at definite temperatures and chilled by immersion in water.

The concentration-temperature diagram indicates the existence of two series of solid solutions (α and β), and of a compound of the composition Al_3Au_8. This compound is found in all alloys containing from 18 to 28 atoms % of aluminium. Recalescence phenomena associated with the cooling curves of alloys containing from 10 to 27 atoms % of aluminium point also to the formation of a compound, $AlAu_4$. The relations between the solid phases are discussed with reference to an extensive series of microphotographs.   H M D

Mineralogical Chemistry.

Mixed Carbonates from Traversella. MARIO DELGROSSO (*Atti Accad. Sci. Torino*, 1914, **49**, 1106—1117. Compare A., 1913, ii, 5).—The author has analysed a number of specimens from the Traversella deposits containing calcium, magnesium, and ferrous carbonates, together with small proportions of extraneous matter. The presence of ferrous carbonate is not always recognisable from external characters, the most nearly colourless rhombohedral crystals often containing this carbonate in large proportions. In only one instance, where the conditions of deposition were evidently abnormal, was there any marked divergence from the relation $CaCO_3 = MgCO_3 + FeCO_3$. The conclusion is drawn that these minerals represent isomorphous mixtures of typical dolomite with typical ankerite.   T. H. P.

Melilite and Other Minerals from Gunnison Co., Colorado. ESPER S. LARSEN and J. FRED HUNTER (*J. Washington Acad. Sci.*, 1914, **4**, 473—479).—A complex of coarse-grained alkaline igneous rocks cuts near Cebolla and Beaver Creeks in the Uncompahgre Quadrangle, Colorado. One of these rocks, named uncompahgrite, is composed largely of melilite, together with pyroxene, perovskite, magnetite, and apatite. The melilite, occurring as large cleavage plates reaching a foot across, is colourless to grey with a greasy lustre, and closely resembles nephelite in appearance. It gelatinises only with weak acids; analysis gave I, D 2·98 (after deducting all amounts of apatite, calcite, magnetite, and perovskite). Two types of alteration of the melilite are recognised: most frequently it is altered to a fine aggregate of garnet, diopside, idocrase, etc.; and at other times to the new mineral cebollite (see following abstract):
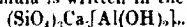
	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
I. 44·53	—	10·80	—	2·04	0·16	34·63
II. 4·29	5·08	4·46	24·09	—	—	31·06

	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	4·35	3·40	trace	0·49	100·00
II.	0·52	—	—	—	99·51

Analysis II is of a black, titaniferous andradite from a soda-syenite allied to ijolite. A description is given of the perovskite found in these rocks, and also of anatase occurring as large, dark and translucent crystals on the joint planes of a diorite dyke.   L. J. S.

Cebollite, a New Mineral. ESPER S. LARSEN and W. T. SCHALLER (*Washington Acad. Sci.*, 1914, **4**, 480—482).—This mineral occurs as an alteration product of melilite at Beaver Creek, Gunnison Co., Colorado (see preceding abstract). It forms a dull, compact, white

to greenish fibrous aggregate; D 2·96, hardness 5. The
characters of the minute fibres suggest orthorhombic system.
The following analysis (after deducting 18·05% insoluble,
admixed diopside, garnet, idocrase, etc.) gives the formula
H₄Al₂Ca₅Si₃O₁₆. Since the powdered mineral in water is
alkaline with phenolphthalein, the group (CaOH) is taken to
be absent, and the formula is written in the form:

$$(SiO_4)_3Ca_5[Al(OH)_2]_2.$$

The mineral gelatinises with acids, and is perhaps related to the
zeolites.

SiO₂	Al₂O₃	Fe₂O₃	FeO	CaO	MgO	Na₂O	K₂O	H₂O
33·02	14·02	3·43	0·21	35·72	4·39	2·57	trace	

L. J. S.

Analytical Chemistry.

Apparatus for the Analysis of Complex Gas Mixtures.
GUY B. TAYLOR (*J. Ind. Eng. Chem.*, 1914, **6**, 845—848).—In the
apparatus described the Bone and Wheeler method of combustion
tion (A., 1908, ii, 221) is combined with the usual gas
compensation burette, a copper oxide U-tube for the estimation of
hydrogen and carbon monoxide, and a slow combustion burette for
burning hydrocarbons. The absorption vessels dip into a mercury
trough; the reagents are introduced by means of curved pipes
under the lower edge of the absorption vessels, and after use are
discharged by the aid of a suction apparatus. A trustworthy
method for the separation of carbon monoxide, hydrogen, methane
and ethane is given.   W. P.

New Method for the Precise Standardisation of Hydro-
chloric Acid Solutions. LAUNCELOT W. ANDREWS (*J. Amer.*
Soc., 1914, **36**, 2089—2091).—The following method for standardising
solutions of hydrochloric acid depends on the loss of weight due
by the conversion of silver nitrate into the chloride; its accuracy
is only limited by the errors of weighing.

Two similar silica or porcelain dishes, of 75—100 c.c. capacity,
are taken, each provided with a light cover and one of them with
a stirring rod, short enough to lie under the cover. The dish
without a rod is referred to as the "companion dish." Into the
other are placed about 2 grams of pure silver nitrate. Both dishes
are put into an oven at 160°, and the temperature is raised so
until the weight is constant. Fifty c.c. of 0·2N-hydrochloric acid
to be standardised are placed in each dish, the temperature of the
solution when measured being noted. The silver nitrate is stirred
up with the solution until it has dissolved and the silver chloride

Both dishes are heated at 95—100°, finally dried at ... cooled in the desiccator, and weighed. The increase in the ... of the companion dish represents the weight of non-volatile ... contained in the acid, and its amount is deducted from ... weight of the silver chloride. The normality of the solu-... is given by the expression $N = (W - W_1 + w_1 - w)/(0.026551)$, ... V is the corrected volume of the solution, W the weight of ... silver nitrate and dish, W_1 the weight of the silver chloride, ... nitrate, and dish, w the weight of the companion dish before ... experiment, and w_1 its weight at the close of the experiment.

E. G.

Estimation of Iodine in Connexion with Studies in ... Thyroid Activity   E. C. KENDALL (*J. Biol. Chem.*, 1914, 19, ...—56. Compare A., 1912, ii, 864).—The author gives addi-... details and slight modifications of his process for estimating ... in the presence of chlorides, bromides, and organic matter.

H. W. B.

Oxidation of Sulphur Compounds of Coal, and of Nitro-... in the Bomb Calorimeter, and the Correction to be ... in Estimating the Heat Value of Coal.   SAMUEL H. ... (*J. Ind. Eng. Chem.*, 1914, 6, 812—822).—When the ... sulphur compound of coal, pyrites, is burned with a non-... fuel in the calorimeter in an atmosphere of oxygen ... pressure, a fairly stable condition results. This condition is ... between the practically complete conversion to sulphur ... existing under the conditions of equilibrium at ordinary ... temperatures, and the almost total absence of sulphur trioxide ... of combustions without a catalyst to convert the ... dioxide into sulphur trioxide as the temperature falls. ... relative amount of sulphur converted into sulphur trioxide ... with the amount of nitrogen oxides formed in the bomb. ... nitrogen of coal is much more efficient in forming nitrogen ... than is the nitrogen of the bomb gases; this, in connexion ... fact that in ordinary work the concentration of nitrogen in ... gases before ignition is at least 5%, accounts for the ... complete oxidation of the sulphur in coal to sulphur ... Much too low results are obtained when coal containing ... equivalent to about 7% of sulphur is burned at 20 atmo-... pressure with 0.53% of nitrogen in the bomb gases. With ... percentages of nitrogen the results are more trustworthy. ... in burning coal with less than 2% of sulphur in a bomb ... from which the air is not removed previously, there ... sufficient formation of nitrogen oxides to ensure almost ... oxidation of the sulphur. The heating value of sulphur ... found to be 4975 cal. per gram.   W. P. S.

Chief Cause of the Loss of Sulphur Trioxide and of ... Chlorine by Incinerating Substances Containing these ... Constituents. JAMES O'SULLIVAN (*Analyst*, 1914, 39, 425—428).—... the incineration of substances containing chlorides the latter

are decomposed and chlorine is lost, but no reduction take[...]
in the quantity of calcium, potassium, and sodium sulphates[...]
may be present. Magnesium sulphate undergoes decomposition[...]
ignition unless a carbonate is present; in the absence of a carbon[...]
magnesium sulphate is converted entirely into magnesium [...]
If present in sufficient quantity in a substance containing c[...]
magnesium sulphate may cause the whole of the chlorine to [...]
when the substance is incinerated.   W. P [...]

Presence of Sulphates in Flour. R. A. Cripps and A.
Wright (*Analyst*, 1914, **39**, 429).—The quantity of sulphate[...]
found in the ash of flour, amounting to about 0·02% of the w[...]
of the ash, does not represent the amount of sulphates in the f[...]
since, during ignition, the hydrogen phosphates present decom[...]
the sulphates with loss of sulphuric acid. From 0·0069 to 0·[...]
of sulphur trioxide is found if the flour is extracted with d[...]
acetic acid and the sulphate precipitated in the solution by [...]
addition of barium chloride, after the proteins have been remo[...]
by means of tannin solution.   W. P [...]

**Calcination of Magnesium Ammonium Phosphate [...]
Causes of its Blackening.** José Gibal Pereira (*Anal. Fis[...]
1914, **12**, 109—112).—The darkening of this phosphate on calci[...]
tion is due in all cases to organic matter, which also determines [...]
eventual formation of phosphides. In the absence of orga[...]
matter, the calcined substance remains quite colourless. G. D [...]

**Estimation of Carbon in Steel by the Direct Combustion
Method.** Wm. Brady (*J. Ind. Eng. Chem.*, 1914, **6**, 843—[...]
The method consists in the direct combustion of the stee[...]
oxygen; the carbon dioxide produced is absorbed in a kno[...]
excess of barium hydroxide solution. When the combustio[...]
completed, the barium carbonate and excess of barium hydr[...]
are rinsed into a flask, and the hydroxide is titrated with stand[...]
ised hydrochloric acid, using phenolphthalein as indicator. [...]
oxygen used is passed through potassium hydroxide solution a[...]
soda-lime, and a tube containing granulated zinc is placed betwe[...]
the combustion tube and the absorption apparatus to prevent an[...]
sulphuric acid resulting from the oxidation of sulphur from pass[...]
into the barium hydroxide solution.   W. P [...]

**Estimation of Carbon in Steels and Irons by Direct Com
bustion in Oxygen at High Temperature.** J. R. Cain and H. E.
Cleaves (*J. Washington Acad. Sci.*, 1914, **4**, 393—397).—In the
ordinary method of estimating carbon in steels, etc., by combustion
in oxygen, small additional quantities of carbon are obtained whe[...]
the oxides are powdered and again heated in oxygen. The author[...]
in place of the latter procedure, increase the heat of the furnace
after the metal has been oxidised as far as possible under the usual
conditions, and maintain the oxides in a state of fusion for about
thirty minutes. In this way it was found that some steels giv[...]

more carbon and others give decidedly more, whilst with the increase amounts to nearly 0·02%. The barium carbonate method (this vol., ii, 577) was used for the estimation of carbon dioxide.
W. P. S.

Perchloric Method of Estimating Potassium, as Applied to Water Analysis. CLARENCE SCHOLL (*J. Amer. Chem. Soc.*, 1914, 36, 2483).—The method of estimating potassium as the perchlorate has been studied and proved to be accurate. Sulphates and ammonium salts must be eliminated before applying the test, phosphates do not introduce any error, and therefore need not be removed.

The method as modified for use in water analysis is as follows: a measured quantity of the water is evaporated to 150 c.c., 10 c.c. concentrated hydrochloric acid are added, and the liquid is heated until it boils. Barium chloride solution (10%) is now introduced drop by drop until all the sulphates are precipitated, and after boiling for fifteen minutes the solution is filtered, the filtrate evaporated to dryness, and the residue heated until all the ammonium salts have been expelled. The residue is dissolved in 20 c.c. of water, a slight excess of 20% perchloric acid solution added, and the solution evaporated to dryness. If white fumes do not appear, the residue is redissolved in 10 c.c. of water, again treated with perchloric acid, and evaporated to dryness; this process is repeated until white fumes appear. The residue is now treated with 15 c.c. of 96—97% alcohol containing 0·2% of perchloric acid, broken up with a stirring rod, collected in a Gooch crucible, repeatedly washed with the alcoholic solution of perchloric acid, dried at 120—130°, and weighed.

This method is rapid, simple, inexpensive, and accurate. E. G.

Estimation of Zinc in Treated Wood. M. HUME BEDFORD and E. PRASSTIEL (*J. Ind. Eng. Chem.*, 1914, 6, 811).—The following method is recommended for the estimation of zinc in red oak which has been treated with zinc chloride. Three grams of the sawdust, dried at 110° are mixed with 35 grams of sodium peroxide and fused in a bomb. The mass is then dissolved in water, the liquid is acidified with hydrochloric acid, boiled, and 2 grams of tartaric acid, 10 c.c. of concentrated nitric acid, and 5 c.c. of 8% barium chloride solution are added. The mixture is rendered alkaline, 15 c.c. excess of concentrated ammonia are added, and, after diluting to 400 c.c., the zinc is titrated at 80° with standardised potassium ferrocyanide solution.
W. P. S.

Detection of Lead in Toxicology, Particularly in Urine in Cases of Lead Poisoning. G. MEILLÈRE (*J. Pharm. Chim.*, 1914, [viii], 10, 225—231).—Small quantities of lead in solution may be detected by adding copper sulphate to the solution, precipitating the metals with hydrogen sulphide, dissolving the mixed sulphides in nitric acid, and then separating the lead from the copper electrolytically. In the case of urine, the quantity voided during twenty-four hours is treated with 1% of its volume of hydrochloric acid,

1 gram of copper sulphate is added, and the mixture is treated with hydrogen sulphide. The precipitate is collected on a filter, washed, then dissolved in nitric acid, the solution evaporated, and the residue heated until the copper nitrate is converted into oxide. This residue is dissolved in 6 c.c. of nitric acid, the whole is diluted to 100 c.c., and submitted to electrolysis. Small platinum electrodes are employed; the whole of the lead is deposited on the anode within twenty-four hours by using a current at a voltage of such amperage that there is but a slight evolution of gas at the anode. The deposit of lead peroxide may be weighed, or it is identified by dissolving it in nitric acid containing oxalic acid and applying suitable tests to the solution. W. P.

Method of Estimating Small Quantities of Lead in Solder, etc. PIERRE BRETEAU and PAUL FLEURY (*J. Pharm. Chim.*, 1914, [vii], **10**, 265—273. Compare this vol., ii, 77). The solder is fused with a mixture of sodium carbonate and sulphur; the mass is treated with boiling water, and the lead, copper, and iron sulphides are collected on a filter. These sulphides are then dissolved in hydrochloric acid containing bromine, the solution treated with sulphurous acid to reduce the iron, and, after a few minutes, potassium cyanide and potassium hydroxide are added. On the addition of sodium sulphide to the alkaline solution copper lead to be precipitated as its sulphide, whilst the iron and the remain in solution. The lead sulphide is collected, dissolved in dilute nitric acid, the solution evaporated, and the residue heated for one hour at 150°. The residue is then dissolved in acetic solution again evaporated, and heated. The lead nitrate obtained is dissolved in 5 c.c. of water, a small crystal of sodium acetate is added, and the solution is poured slowly into a slight excess of standard potassium dichromate solution; the dichromate solution must not be added to the lead solution. The lead chromate is then collected on a filter, washed with water, and the excess dichromate is estimated in the filtrate. The potassium dichromate solution may conveniently contain 0·1432 gram of the salt per litre; 5 c.c. of this solution are equivalent to 0·001 gram of lead. The copper and iron may be estimated by the usual methods in the filtrate from the lead sulphide after the hydrogen sulphide has been expelled by boiling the solution with the addition of sulphurous acid. W. P.

Separation of Vanadium and Phosphorus with "Cupferron" VICENTE GARCÍA RODEJA (*Anal. Fis. Quim.*, 1914, **12**, 375—382). After reduction of the vanadate to the hypovanadate, the vanadium is quantitatively precipitated by freshly prepared cupferron solution, and the phosphate may be estimated in the filtrate. G. B.

An Arrangement for the Detection of Residual Acetylene Hydrocarbons in Caoutchouc. L. LUTZ (*Chem. Zentr.*, 1914, ii, 102; from *Bull. Sci. Pharmacol*, 1914, **21**, 193—195).—An arrangement of a flask fitted with a delivery tube, bent twice

at angles, is described, in which finely cut caoutchouc may be ... with water so that, while the water is condensed in the first ... tube, any volatile hydrocarbons pass over into a suitable ...

J. C. W.

Hydrogen Number of Some Essential Oils and Essential ... Products. I. Oils of Sassafras, Anise, Fennel, Clove, ... Pimento. ALAN R. ALBRIGHT (*J. Amer. Chem. Soc.*, 1914, **36**, ...)—Fokin (A., 1908, ii, 637) has suggested the determination of hydrogen numbers for unsaturated compounds corresponding with the iodine numbers of Hübl and Wys. It has now ... found that a hydrogen number can be assigned to certain ... oils, colloidal palladium being used as the catalyst. Some ... especially those with a constituent containing an allyl or ... yl group, are capable of very rapid hydrogenation. Such ... are so rapidly reduced that, in the case of an oil con... one of them, the allyl or propenyl groups are quantitatively ... before other configurations are attacked to more than ... extent. The hydrogen number of the oil is defined as the ... of c.c. of hydrogen at 0° and 760 mm. which are absorbed ... gram of the oil during the period of most rapid absorption of ...

... order to determine the hydrogen numbers of the oils of ..., anise, fennel, clove, and pimento, experiments were first ... with the active constituents of the oils, namely, safrole, ... and eugenol. Imitation oils were then prepared contain... particular active constituent in the proportion in which it ... in the natural oil, the remainder being represented by ... As limonene itself absorbs hydrogen fairly rapidly, the ... afforded a somewhat severe test of the hydrogenation ... determination. Samples of commercial oils were subse... submitted to the hydrogenation process. The hydrogen ... of the various substances and oils are recorded. E. G.

New Reaction for Resorcinol. PARIDE TORTI (*Boll. Chim. ...*, 1914, **53**, 265).—When a little resorcinol is heated with a few ... of nitric acid (D 1·40), an intense red coloration is formed. ... reaction is visible with as little as 0·00025 gram of resorcinol, ... forty times as sensitive as the reaction with ferric chloride. ... cool, the liquid deposits minute, reddish-brown, acicular ... which are soft to the touch, and dissolve in water, ... ether, or chloroform. T. H. P.

Estimation of Sugar in Blood. PHILIP A. SHAFFER (*J. Biol. ...*, 1914, **19**, 285—295).—A method is described for estimating ... sucrose in 5 c.c. of blood. Its essential features consist in ... the proteins by combined heat coagulation and the ...-Rona colloidal iron precipitation, and, after heating with ... solution, estimating the cuprous oxide formed, by ... permanganate method or by simply dissolving the oxide ... acid, treating with ammonia, and comparing with a

standard ammoniated copper solution in a colorimeter. [illegible]
the processes, including the reduction, are carried out in [illegible]
tubes, and the precipitates collected and washed by centrifugation.
tion.

The method previously described, involving the use [illegible]
alcohol for the precipitation of the proteins in the blood [illegible]
lower results for the blood sugar, and is therefore [illegible]
unsatisfactory.   H. W. B.

Estimation of Aldoses. I. The Action of Neutral Sodium
Hypoiodite. N. BLAND and L. L. LLOYD (*J. Soc. Chem. Ind.*,
1914, **33**, 948 949).—In the examination of the action of a [illegible]
on sodium hypoiodite, it was found that the reaction with the
aldehyde proceeds quantitatively according to the [illegible]
$NaIO + CH_2O = NaI + H \cdot CO_2H$, and may be used for the [illegible]
of the aldehyde in aqueous solution.   Five c.c. of commerce
formalin are diluted to 1 litre, and 10 c.c. of this solution is
added to 50 c.c. of $N/10$-iodine solution, previously [illegible]
slightly alkaline with sodium hydroxide.   After five minutes a
mixture is acidified with sulphuric acid, and the liberated [illegible]
is titrated with thiosulphate solution.   Untrustworthy results are
obtained when the method is applied to paraformaldehyde [illegible]
acetaldehyde.

In the case of sugars, neutral sodium hypoiodite oxidises
the aldehyde group; for instance, the aldehyde group in dextrose
requires one molecule of iodine or hypoiodite.   Lævulose and
sucrose contain no aldehyde group, and do not react with [illegible]
hypoiodite, but the latter sugar, on inversion, yields dextrose and
lævulose, and requires one molecule of iodine.   The following
results were obtained with different sugars; in each case, [illegible]
of a 1% solution of the sugar were added to a mixture of [illegible]
of $N/10$-iodine solution and 50 c.c. of $N/10$ sodium hydroxide
solution (this produces a neutral solution); after five minutes'
contact, the solution was acidified, and the liberated iodine titrated
Dextrose, 96·4 to 99·7%; lactose, 99·1 to 99·4%; maltose, 99·1
101·8%; sucrose (after inversion), 100·8 to 101·3%; lactose (after
inversion), 99·1 to 99·4%; maltose (after inversion), 99·1 to 99·9
                                                             W. P. S.

Estimation of Pentosans.   J. VAN HAARST and S. C. J. [illegible]
(*Chem. Weekblad*, 1914, **11**, 918—925).—A comparison of results
obtained in the estimation of pentosans by Tollens's method and
that given in the Dutch "Codex Alimentarius."   The authors
commend distilling with hydrochloric acid at the standard rate
400 c.c. in two hours.   A slower rate tends to decompose [illegible]
the furfuraldehyde, while more rapid distillation fails to [illegible]
complete decomposition of pentosans containing arabinose.   The
results obtained by Tollens's method are more accurate than [illegible]
given by the process of the "Codex Alimentarius," but none
the published tables for calculating the amount of the pentose
gives the velocity of distillation employed in their compilation
                                                             A. J. W.

Estimation of Hydrogen Cyanide in Feeding Stuffs, and Occurrence in Millet and Guinea Corn. J. R. Furlong (*Analyst*, 1914, **39**, 430—432).—The method consists essentially in conversion of the hydrogen cyanide into Prussian blue, and estimation of the latter colorimetrically. One hundred grams of the ground substance are extracted for three hours in a Soxhlet apparatus with 90% alcohol. The extract is transferred to a flask, and after the alcohol has been distilled off, 150 c.c. of 10% tartaric acid are added, and the distillation is continued, the distillate being collected in a receiver containing 5 c.c. of 10% potassium hydroxide solution. After one hour the receiver is changed, water is added to the flask, and a second quantity of distillate collected. These operations are repeated until the evolution of hydrocyanic acid ceases. The distillate is concentrated to 50 c.c., boiled for ten minutes with the addition of 1 c.c. of 20% ferrous sulphate solution containing 1% of ferric chloride, cooled, acidified with hydrochloric acid, and 10 c.c. of glycerol are added. After about fifteen hours, the mixture is diluted with water to 50 c.c., and the blue coloration compared with that given by known quantities of hydrogen cyanide under similar conditions. When the amount of hydrogen cyanide present is not less than 0·001 %, the standards may be made up directly, but with smaller quantities it is necessary to dilute to 150 c.c. and then concentrate, as in the preparation of the solution from the substance under examination. Estimations of hydrogen cyanide in millet and guinea-corn plants of various ages showed that all the young plants contained a cyanogenetic glucoside, whilst the full-grown plants were free from this substance. In the case of guinea corn, the yield of hydrogen cyanide reached a maximum (0·01%) in the young plants, and decreased as growth proceeded. With millet the maximum amount (0·045%) was found in the plants which attained a height of 24 inches. W. P. S.

Cause of Acidity of Fresh Milk of Cows and a Method for Determination of Acidity. Lucius L. van Slyke and Alfred W. Bosworth (*J. Biol. Chem.*, 1914, **19**, 73—76).—The acidity of fresh milk is due to the presence of acid phosphates. Addition of alkali to milk leads to the hydrolysis of the calcium present, so that by the direct titration of milk with alkali, using phenolphthalein as indicator, results are obtained for the acidity which may be twice as great as they should be. The calcium must, therefore, be removed before titrating with the alkali by treating 100 c.c. of milk with 2 c.c. of a saturated solution of normal potassium oxalate, and keeping the mixture for less than two minutes. H. W. B.

Sulphocarbon Oil. F. Canzoneri and G. Bianchini (*Ann. Chim. Applicata*, 1914, **2**, 1—9).—The authors describe the composition, properties, and means of detection in mixtures of the so-called "sulphocarbon" oil, that is, olive oil extracted by means of carbon bisulphide. T. H. P.

Specific Reaction of Oils of Marine Animals and **the Products of Hydrogenation.** M. TORTELLI and E. JARRI in *Chim. Applicata.* 1914. **2**. 80—98).—The reactions pr‑viously described as specific for the oils and fats of marine animals are due to ties or to products of alteration which may be eliminated by the purification, and may also be found in fats and oils of trial or vegetable origin. The authors find, however, that the following test is given by the oils and fats of marine animals is by no others; the quantities in brackets represent the portions to be taken in examining a fat obtained by catalytic hydrogenation. Into a graduated cylinder of about 15 mm. internal diameter and 15 c.c. (25 c.c.) in capacity, and fitted with a glass stopper, are introduced 1 c.c. (5 c.c.) of the oil or melted fat, 2 (10 c.c.) of chloroform, and 1 c.c. (1 c.c.) of glacial acetic acid, which are shaken to give a homogeneous mixture. When 30 40 drops (2·5 c.c.) of a 10% solution of bromine in chloroform are vigorously agitated for a few seconds, the cylinder being placed on a sheet of paper. If the oil is derived from a marine animal, the liquid becomes first red and, within a minute, green, the colour increasing in intensity for some time and remaining constant for an hour. The coloration is formed rapidly with highly refined oils, and varies from green with yellowish reflection to green with a bluish reflection, according to the origin of the oil. In the case of a hydrogenated oil, the first coloration is reddish-yellow, and the final intense green colour is obtained with greater rapidity than with the non-hydrogenated oils.

The reaction serves for the detection of the presence in alimentary fats of synthetic fats prepared from the oils of marine animals.   T. H. P.

Drying Urine for Chemical Analysis. WINFRED W. Lord (*J. Biol. Chem.*, 1914, **19**, 105—113).—In drying urine of herbivora for the determination of the heat of combustion it is found that large quantities of ammonia and carbon dioxide are evolved. The methods used to remove the water are (1) to use a desiccator over sulphuric acid at about 5 mm. pressure and temperature, and (2) to pass over the sample a current of air free from ammonia and carbon dioxide. The loss of nitrogen under these conditions may amount to as much as 50%, of the total nitrogen of the urine, and arises mainly from the decomposition of ammonium carbonate, and not of urea or hippuric acid. The carbon dioxide is lost in a quantity more than sufficient to combine with the ammonia lost to form the normal carbonate.

The author estimates the total carbon and total hydrogen (including that of the water) in the fresh undried urine by combustion in an ordinary combustion furnace; this method gives concordant results.   H. W. B.

A Permanent Preparation of Urease, and its Use in the Estimation of Urea. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1914, **19**, 211—228).—Urease in powder from
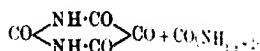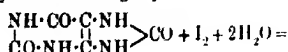
...red by **extracting soja bean** meal with water at room temperature, and then **pouring the clear** extract into at least ten times volume of **acetone.** The precipitated urease can be dried in vacuum, and **maintains its** activity for an apparently indefinite period. It is soluble in water, and the solution, if kept at 0°, does [not] lose its activity for several weeks, especially if 5% of dipotassium hydrogen phosphate is also present in the solution.

For estimating **urea in urine,** one-half c.c. of urine is mixed with 1 c.c of 0.6% potassium dihydrogen phosphate and 1 c.c. of a 10% solution of urease. After twenty minutes at 15°, or three minutes at 5°, to complete the decomposition of the urea, 4 to 5 grams of potassium carbonate **are added,** and the ammonia then aspirated into 25 c.c. of $N/50$-hydrochloric or sulphuric acid. When the action is finished, the excess of acid is titrated with $N/50$-alkali. Urease is a particularly valuable reagent because it enables a rapid estimation of the urea in the blood to be made, its action being so specific that no other constituent of the blood is attacked. The original paper must be consulted for the details of the methods and apparatus recommended by the authors.　H. W. B.

Estimation of Uric Acid in Urine. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1914, **53**, 257-262).– In the author's method the following solutions are employed: (1) Salkowski-Ludwig reagent, prepared by mixing equal volumes of (*a*) and (*b*) immediately before using: (*a*) 26 grams of silver nitrate are dissolved in 300 c.c. of distilled water, and ammonia solution added until the brown precipitate at first formed dissolves completely, the whole being then made up to 1 litre with water; (*b*) 100 grams of sodium chloride and 150 grams of ammonium chloride are dissolved in about 500 c.c. of distilled water, ammonia solution in excess added, and the volume made up to 1 litre. (2) Aqueous 2% lead acetate prepared in the hot; this serves as a defecating and clarifying agent, mucinoid substances and uranyl phosphate being precipitated, together with pigmentary matter. (3) Decinormal solution containing 25 grams of potassium iodide per litre. A 0.1% aqueous solution of indigo-carmine. The procedure is as follows:

Two hundred c.c. of the urine are mixed with 20 c.c. of the lead acetate solution, and the liquid at once poured on to a dry folded filter. Sixty c.c. of the filtrate are introduced into a 100 c.c. flask containing 10 c.c. of the Salkowski-Ludwig reagent, the mixture being well stirred, and, after a short time, the precipitate collected quantitatively on a small filter, and washed three or four times with water. Most of the precipitate is then returned to the precipitation vessel by means of a glass rod, and treated with about 50 c.c of a solution of 2 grams of potassium iodide in 150 c.c. of water. The turbid liquid thus obtained is then poured through the filter containing the remainder of the precipitate, which is washed several times with the potassium iodide solution. The filtrate, consisting of about 150 c.c. of colourless, almost clear liquid, is acidified by the addition of a drop or two of acetic acid, and

rendered alkaline by means of about 5 grams of [illegible]
The solution is then made slightly but distinctly [illegible]
more drops of the indigo-carmine solution, and is [illegible]
shaken with decinormal iodine solution until a single [illegible]
immediate change from blue to yellowish-green. The [illegible]
c.c. of decinormal iodine used, multiplied by 0.0[illegible]
amount of uric acid in grams per 100 c.c. of the [illegible]
accuracy of the method has been tested by means of both [illegible]
solution of pure potassium urate and urines containing [illegible]
added proportions of uric acid.

The action of iodine on uric acid in presence of borax is [illegible]
by the following equation :

$$\begin{array}{l} NH\cdot CO\cdot C\cdot NH \\ CO\cdot NH\cdot C\cdot NH \end{array}\!\!>\!CO + I_2 + 2H_2O =$$

$$CO\!<\!\begin{array}{l} NH\cdot CO \\ NH\cdot CO \end{array}\!\!>\!CO + CO\cdot NH_{[illegible]}$$

The alloxan thus formed is also acted on by the iodine [illegible]
action is so slow as to be virtually negligible; the same is the [illegible]
with the purine derivatives, other than uric acid, occurring [illegible]
                                                    T H P

Separate Estimations of the Purine Substances and
Uric Acid in Urine. DOMENICO GANASSINI (*Boll. Chim.* [illegible]
1914, **53**, 262—265).—This method is based on the fact that
silver-magnesium precipitate yielded by the Salkowski-[illegible]
reagent is, when thoroughly washed and suspended in [illegible]
neutral towards phenolphthalein. When, however, highly con-
trated aqueous potassium iodide is added, the precipitate [illegible]
almost completely, and the liquid becomes intensely alkaline [illegible]
to the formation of normal potassium urate and of the potas.
salts of the other purine derivatives present. The alkalinity of
liquid is, therefore, directly proportional to the content of the
compounds, inclusive of the uric acid. The latter may also [illegible]
be estimated separately in the same liquid by the method [illegible]
described (preceding abstract).

The procedure is at first similar to that used in the estimate
uric acid alone (*loc. cit.*), with the exception that the precip
given by the Salkowski-Ludwig reagent is washed with dis-
water until the washing water fails to react alkaline with phe
phthalein or litmus. The solution of this precipitate in the po
ium iodide solution, amounting to about 150 c.c.. is titrated
$N/20$-sulphuric acid solution in presence of 5—6 drops of [illegible]
holic phenolphthalein. Four or five grams of potassium hydr
carbonate and 10 drops of 0.1% indigo-carmine solution are th
added to the liquid, which is titrated with $N/10$-iodine solu
until the blue colour changes to green. Multiplication of the en
of the number of c.c. of $N/20$-sulphuric acid over that of
$N/10$-iodine by 0.0076 yields the number of grams of purine
pounds, calculated as xanthine, in 50 c.c. of the urine. The [illegible]

... of N/10-iodine, multiplied by 0·0084, gives the grams of ... acid in 50 c.c. of the urine.   T. H. P.

Some New Tests for Veronal. H. Lucas (*Pharm. J.*, 1914, ...).—The odour of iodoform is observed when veronal is ... with aqueous sodium hydroxide, and the resulting solution ... and then warmed with a solution of iodine.

The residue obtained by fusing veronal with sodium hydroxide ... a purplish-violet biuret reaction with a drop of aqueous ... sulphate, and liberates nitrogen (not quantitatively) by ... with concentrated sodium hypobromite.   C. S.

Estimation of Antipyrine. W. O. EMERY and S. PALKIN (*J. Ind. ... Chem.*, 1914, **6**, 751—753).—The method depends on the solu ... iodoantipyrine in chloroform. In the case of antipyrine ... or in such admixture that after treatment with iodine no ... other than iodoantipyrine will be extracted by chloro ... a quantity of the sample containing not more than 0·25 gram ... antipyrine is shaken with 20 c.c. of water, 5 c.c. of alcohol-free ... form, 0·5 gram of sodium hydrogen carbonate, and a slight ... of iodine solution. After a short time, the excess of iodine ... composed by the addition of a few drops of thiosulphate solu ... the iodoantipyrine is shaken out with chloroform, the chloro ... solution is washed with water, filtered, evaporated in a ... flask, and the residue is weighed. The weight of the resi ... multiplied by 0·5992 gives the quantity of antipyrine present. ... the antipyrine is mixed with phenacetin, sulphonal, or ... substance, a weighed portion of the sample is shaken with ... of water, 20 c.c. of concentrated hydrochloric acid, and an ... of iodine solution. After some hours the liquid is decanted ... a glass-wool filter, the tarry residue is washed with 5% ... chloric acid, then dissolved in about 50 c.c. of methyl alcohol ... must be free from ethyl alcohol and acetone), the solution is ... with 50 c.c. of water and sodium hydrogen carbonate, and, ... the excess of iodine has been destroyed by the addition of ... sulphate solution, the iodoantipyrine is extracted with chloro ...   W. P. S.

Use of Manganese Carbonate in the Detection of Traces ... Strychnine. G. GUÉRIN (*J. Pharm. Chim.*, 1914, [vii], **9**, ...).—The author finds that the sensitiveness of the test for ... by means of sulphuric acid and potassium dichromate ... exaggerated, and that the detection of 0·01 mg. by this method ... uncertain. This quantity can be readily detected by the re ... of Mandelin (0·5 gram ammonium vanadate in 100 grams ... pure sulphuric acid), of Wenzell (potassium permanganate ... gram] in pure sulphuric acid [100 grams]), or of Sonnenschein ... tion of the alkaloid in pure sulphuric acid and addition of a ... ... of cerium oxide). According to the author, the last two ... appear to be more sensitive than that first named. ... method which is as sensitive as any of those described above ... in dissolving the alkaloid in two or three drops of sulphuric

acid and adding 2—3 mg. of manganese carbonate. On a ...
blue coloration is developed, which gradually becomes ....
then pink.
H ...

Application of Tungsten Salts to the Analysis of Tan
Materials. ALEXANDER T. HOUGH (*J. Soc. Chem. Ind.*, 1:;;
847—848).—Two reagents, prepared from sodium tungstate, ...
ently give different results (amounts of precipitate) with the ...
tannin, and it is suggested that it may be possible to estae...
purity of a given tannin extract by the constancy of the ...
between the two results. The reagents are prepared as ...
(1) 10% sodium tungstate solution, 5 c.c.; water, 2 ... ;
ammonium chloride solution, 3 c.c.; (2) 10% sodium ....
solution, 5 c.c.; 8% hydrochloric acid, 2 c.c.; 25% am...
chloride solution, 3 c.c. A tannin solution is made ...
about 4 grams of tannin per 250 c.c., and 10 c.c. of this ...
are mixed with 10 c.c. of the first reagent; the mixture ...
on a filter, and 10 c.c. of the filtrate are evaporated to ...
and the residue is weighed (A). The precipitate on the ...
then dissolved in hot water, the solution is added to the ...
of the filtrate, and the whole is evaporated to dryness ...
actual weight of the precipitate is $B - A$; it is necessary ...
tain the weight of the precipitate by this indirect meth...
cannot be washed. A similar estimation is then made ...
second reagent. The amount of precipitate is calculated
percentage of tanning material in the extract, and for ...
pose the quantity of total solids and of tannin (C) in ...
the extract is estimated. Then $100(B - A)/C$ gives the ....
number" of the tannin, using the first reagent; the same ...
gives the "tungstic number," using the second reagent, ...
sumably, "tungstic"/"tungstate" $= K$ for any given ...
material. The author has applied the method only to ...
extract, in which case $K = 1.0503$.   W P ...

Quantitative Estimation of Aspartic and Glutamic A:
in the Products of Protein Hydrolysis. FREDERICK W...
FORRMAN (*Biochem. J.*, 1914, **8**, 463—480).—After hy...
of the protein with hydrochloric acid, the glutamic and as...
acids are converted into their calcium salts, which are then ...
tatively precipitated by the addition of alcohol. After ...
from the alcohol-soluble calcium salts of the other ...
present, the free acids are regenerated by dissolving in water
adding oxalic acid. Traces of accompanying impurities are ...
removed by successive treatment with silver sulphate and ...
tungstic acid. The resulting solution on evaporation ...
crystalline mass, which is now extracted with glacial ace...
The residue consists of a mixture of glutamic and aspart...
and the proportionate quantity of each present is calculated ...
the carbon content of the mixture. As the difference betwee...
percentages of carbon in glutamic and aspartic acids is as gre...
4·73, the proportion can be determined with tolerable accur...

A small quantity of the glutamic acid is transformed into pyrrolidonecarboxylic acid during the preliminary processes indicated above, and is found in the glacial acetic acid extract. It is estimated by measuring the amino-nitrogen before and after boiling in hydrochloric acid, which reconverts the ring compound into glutamic acid.

The actual separation of aspartic and glutamic acids is effected by fractional crystallisation of the copper salts, copper aspartate separating out first. When most of the aspartate has been removed, the larger portion of the glutamic acid is separated by converting it into the hydrochloride.

By means of this method, caseinogen is found to contain 21·77% glutamic acid and 1·71% of aspartic acid, or about twice as much as has hitherto been accepted.   H. W. B.

The **Ferric Alum Estimation of Casein.** H. V. ABNY and H. SCHAEFER (*J. Ind. Eng. Chem.*, 1914, **6**, 748—751).—Two alterations have been made in a method described previously (1913, ii, 407) for the estimation of casein in milk ; to ensure a filtration, the mixture of milk and ferric alum solution is made for one hour before the precipitate is collected, and the titration is made with N/50-thiosulphate solution. The method, as used at present, is as follows. Five grams of milk are treated with 5 c.c. of ferric alum solution (48·2224 grams of $NH_4SO_4)_2,12H_2O$ per litre), and, after one hour, the precipitate collected on a filter and washed until free from soluble iron. The filtrate is treated with 3 c.c. of 31% hydrochloric acid and grams of potassium iodide, heated to 40° for thirty minutes in a closed flask, and the liberated iodine is titrated with N/50-thiosulphate solution. Each c.c. of the ferric alum solution required for the precipitation is equivalent to 0·05934 gram of casein.
          W. P. S.

Comparison of Methods for the Determination of the Proteolytic Activity of Pancreas Preparations. J. H. LONG and A. W. BARTON (*J. Amer. Chem. Soc.*, 1914, **36**, 2151—2166).—The object of this work was to compare the different standards for valuation of the various commercial trypsins or pancreatins. The proteolytic value of six such trypsin preparations has been compared by four distinct methods, namely, the metacasein reaction, the Fuld-Gross sodium caseinate digestion method, the formaldehyde titration of amino-acids produced by digestion, and the fibrin digestion. The results obtained by the four methods agree in placing the activities of the six preparations in the same order, but they do not agree as to relative quantitative value of the different ferments, for the strongest ferment according to the metacasein reaction appears to be about twelve times as strong as the weakest, and according to the fibrin digestion about ten times as strong, whilst by the other tests the relation obtained is as 3 : 1. Still greater irregularities appear in comparing some of the other preparations.

The products sold as trypsins or pancreatins probably contain at least two different enzymes, reacting in different ways with proteins, and the effects produced in any case depend on the proportions in which the enzymes are present. These enzymes possess different degrees of stability towards heat.

It is not at present possible to convert the proteolytic value of a tryptic ferment from the terms of one standard to those of another, since the products are made by very different processes, which probably yield mixtures of ferments in widely different proportions, together with unknown quantities of inorganic salts. A more rational definition of trypsin is desirable, and products should be made to conform to interchangeable standards.   E. G.

Electrical Method of Estimating Salt in Soil. WILLIAM BEAM and GILBERT A. FARAK (*Cairo Sci. J.*, 1914, **8**, 130—.) In estimating the amount of soluble salts in soils by the electrical conductivity method, the error due to the nature of the salts present may be corrected by constructing special tables for the particular combination of salts in the area under examination. The results are especially affected by sodium carbonate, and the resistance is higher when much organic matter is present (Davies and Bryan, *U.S. Dept. Agric. Bur. Soils*, Bull. 61). A more important source of error is that due to the presence of calcium salts (especially sulphate), which is not only harmless, but beneficial in neutralising the effects of toxic salts. This error is avoided by extracting the salts with 40% alcohol instead of water, and comparing the results with those obtained with a solution of salt in the same solvent; calcium sulphate may then be estimated, if desired, by extracting with water as well.

In the case of soils containing moderate amounts of salts, the method usually employed is to treat an amount of soil, containing about 20 grams of dry matter, with 100 c.c. of 40% alcohol, and shake for ten to fifteen minutes. Shaking for one minute gives nearly the same results, and variations, from 38—42%, in the strength of the alcohol are without much influence.

In testing the method with solutions of known concentration, a solution containing 0·030% of gypsum and 0·131% of sodium chloride was found to have a resistance of 210 ohms instead of the calculated resistance of 220 ohms.   N. H. J. M.

Estimation of the Lime Requirement of Soils by means of [Barium Hydroxide]. C. R. MOULTON and P. F. TROWBRIDGE (*J. Ind. Eng. Chem.*, 1914, **6**, 835—837).—The requirement of a soil, as estimated by boiling the soil with an excess of N/10-barium hydroxide solution and measuring the excess by means of the ammonia set free from added ammonium chloride, is proportional to the quantity of barium hydroxide used, and to the acidity of the soil. The result obtained is considerably higher than when the Vietch method is employed. Further, the lime requirement varies with the duration of the distillation and the volume of the distillate until the lime requirement falls to zero (compare Bizzell and Lyon, this vol., ii, 150).   W. P. S.